SUPPORTING INFORMATION

Efficient Synthesis of (*E*)-2-Nitromethylcinnamates via Phosphine-Catalyzed Tandem α-Addition and 1,3-Rearrangement

Guofei Huang,[‡a] Xiaoyu Ren,[‡a] Chunhui Jiang,[ab] Jia-Hong Wu,[a] Guowei Gao[a] and Tianli Wang*[a]

[a] Key Laboratory of Green Chemistry & Technology of Ministry of Education, College of Chemistry, Sichuan University 29 Wangjiang Road, Chengdu 610064 P. R. China. E-mail: wangtl@scu.edu.cn

[b] School of Environmental and Chemical Engineering, Jiangsu University of Science and Technology, 2 Mengxi Road, Zhenjiang 212003 (P. R. China)

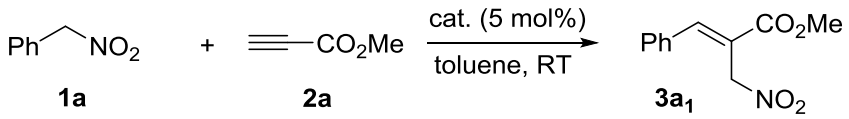
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ or CD_3OD on a Bruker Advance (400 MHz). The chemical shifts are reported in parts permillion (ppm) relative to $CDCl_3$ (δ = 7.26) and to CD_3OD (δ = 3.31) for ^{1}H-NMR and relative to the central resonances of $CDCl_3$ (δ = 77.16) and to CD_3OD (δ = 49.00) for ^{13}C-NMR; spectrometer; Multiplicity was indicatedas follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants (*J*) were reported in Hertz (Hz). All high resolution mass (ESI-MS) were obtained on Thermo LTQ mass spectrometer. For thin layer chromatography (TLC) was performed using commercially prepared and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatographic separations were performed on commercially prepared 200-300 mesh silica gel.

All the substituted nitro compounds were synthesized based on known methods reported in literature.[1]

2. Optimization of Reaction Conditions

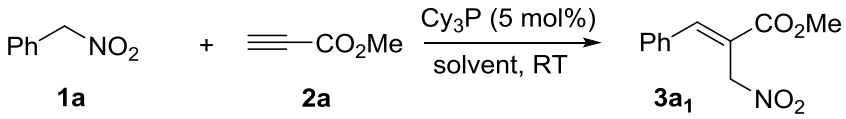
Table S1: Screening of the catalysts[a]



Entry	Catalyst	Time [h]	Yield [%][b]
1	Ph_3P	4	91
2	Ph_2MeP	3	94
3	**Cy_3P**	**1.5**	**95**
4	TEA	4	31
5	DABCO	4	<5

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. [b]Yields of isolated products. TEA = triethylamine, DABCO = 1,4-diazabicyclo[2.2.2]octane.

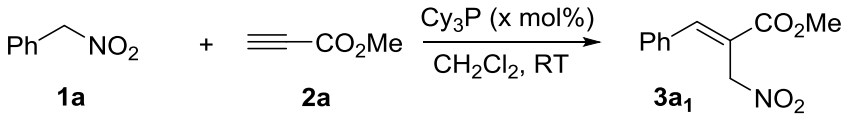
Table S2: Screening of the solvent[a]



Entry	solvent	Time [h]	Yield [%][b]
1	**CH_2Cl_2**	**1**	**95**
2	Toluene	1	92
3	EtOAc	1	41
4	Hexane	1	36
5	MeOH	1	15
6	THF	1	<5
7	Et_2O	1	<5
8	$CHCl_3$	1	90

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. [b] Yields of isolated products.

Table S3: Screening of the catalyst loading[a]

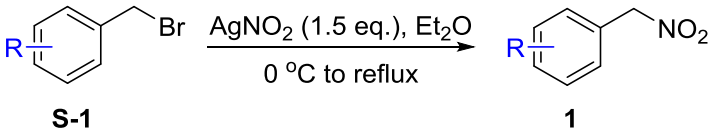


Entry	x mol%	Time [h]	Yield [%][b]
1	5	1	95
2	2	5	95
3	**1**	**12**	**94**
4	0.2	12	11
5[c]	1	12	84

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.15 mmol) and catalyst in solvent (1.0 mL) at room temperature. [b] Yields of isolated products.[c] The solvent was toluene.

3. Preparation of the Substituted Nitromethanes

All substituted nitromethanes were synthesized according to the reported procedures.[1]



Scheme S1. Preparation of the substituted nitromethanes.

Silver nitrite (1.154 g, 7.5 mmol) was added to a round bottom flask covered in tin foil containing anhydrous diethyl ether (15 mL). After stirring at room temperature for 15 minutes, the mixture was then cooled at 0 °C. A solution of benzylbromide (5 mmol) in diethyl ether (1.0 mL) was added dropwise via addition funnel. The reaction was stirred at 0 °C for 1 h and then heated to reflux for 4 h. The mixture was filtered over celite using ethyl acetate as eluent. The product was purified by column chromatography on silica gel (eluting with 10:1 hexane/ethyl acetate unless otherwise stated). All nitro substrates were known compounds and listed in **Figure S1.**

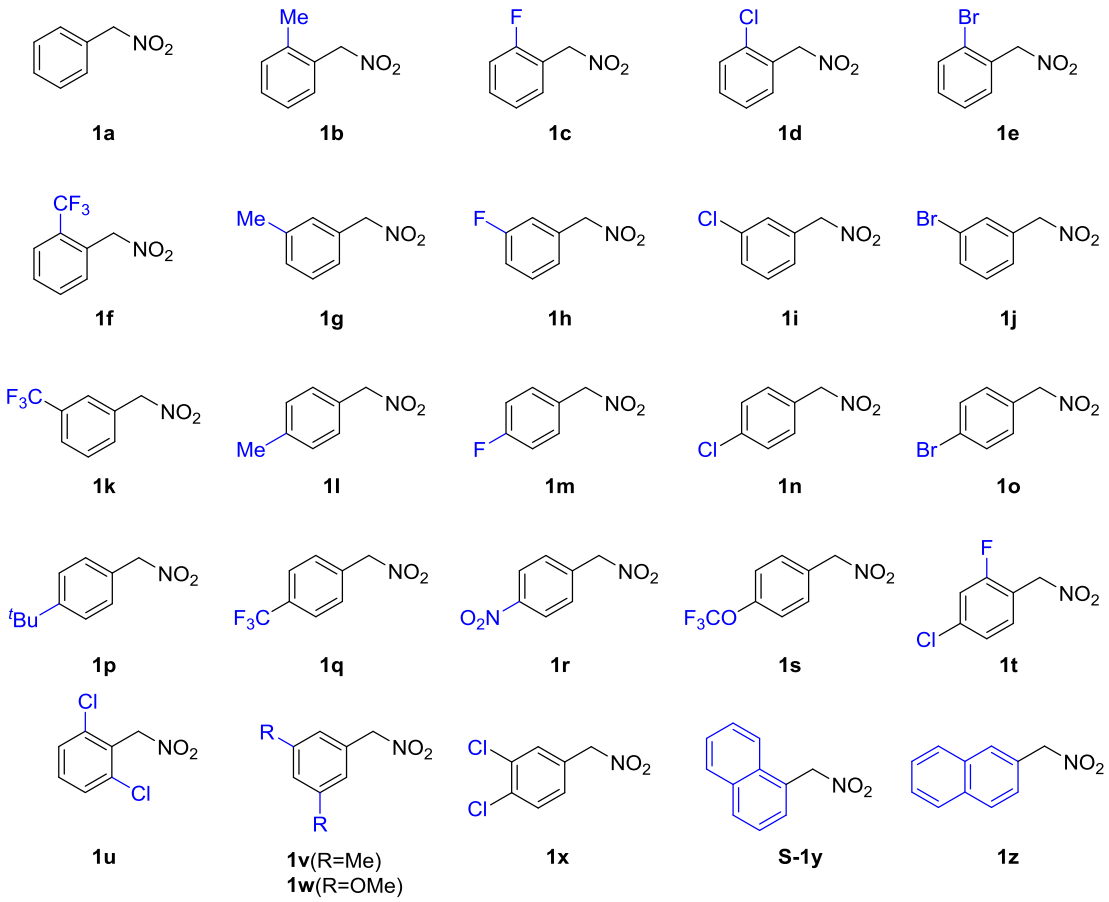
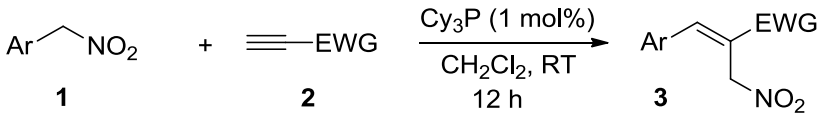


Figure S1. The substituted nitromethanes used in this study.

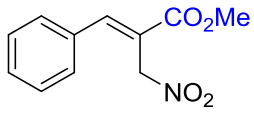
4. Representative Procedure for the Tandem Reaction



To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene **1a** (27.4 mg, 0.2 mmol) and Cy_3P (0.6 mg, 0.002 mmol), followed by the addition of dry CH_2Cl_2 (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate **2a** (25.2 mg, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH_2Cl_2 was removed under reduced pressure. The

residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **3a$_1$** (41.6 mg, 94% yield) as a yellow oil.

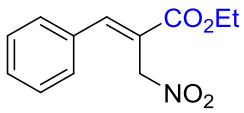
methyl (*E*)-2-(nitromethyl)-3-phenylacrylate (3a$_1$)



3a$_1$

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.48-7.41 (m, 3H), 7.36-7.23 (m, 2H), 5.35 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.20, 147.66, 133.48, 130.20, 129.13, 128.91, 122.00, 71.83, 52.72; HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NO_4$ $[M+Na]^+$ = 244.0586, found = 244.0568.

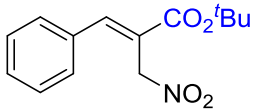
ethyl (*E*)-2-(nitromethyl)-3-phenylacrylate (3a$_2$)



3a$_2$

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.48-7.41 (m, 3H), 7.36-7.29 (m, 2H), 5.35 (s, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.69, 147.33, 133.58, 130.11, 129.10, 128.89, 122.34, 71.87, 61.83, 14.15; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}NO_4$ $[M+Na]^+$ = 258.0742, found = 258.0732.

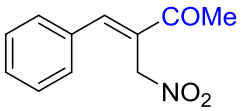
***tert*-butyl (*E*)-2-(nitromethyl)-3-phenylacrylate (3a$_3$)**



3a$_3$

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.46-740 (m, 3H), 7.34-7.29 (m, 2H), 5.30 (s, 2H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.62, 146.41, 133.82, 129.86, 129.04, 128.79, 123.81, 82.52, 72.10, 27.98; HRMS (ESI) *m/z* calcd for $C_{14}H_{17}NO_4$ $[M+Na]^+$ = 286.1055, found = 286.1029.

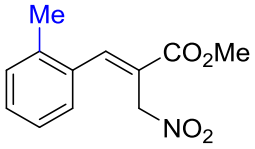
(*E*)-3-(nitromethyl)-4-phenylbut-3-en-2-one (3a$_4$)



3a$_4$

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.52-7.42 (m, 3H), 7.37-7.30 (m, 2H), 5.34 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.47, 147.10, 133.51, 131.25, 130.34, 129.22, 128.87, 70.63, 25.33; HRMS (ESI) *m/z* calcd for $C_{11}H_{11}NO_3$ $[M+Na]^+$ = 228.0637, found = 228.0628.

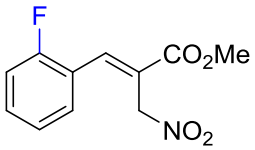
methyl (*E*)-2-(nitromethyl)-3-(o-tolyl)acrylate (3b)



3b

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.32 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.28-7.20 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 1H), 5.24 (s, 2H), 3.88 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.97, 147.35, 137.25, 132.82, 130.60, 129.99, 127.79, 126.37, 122.86, 71.69, 52.70, 19.88; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}NO_4$ $[M+Na]^+$ = 258.0742, found = 258.0728.

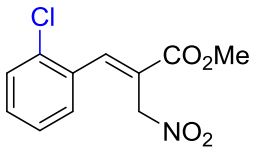
methyl (*E*)-3-(2-fluorophenyl)-2-(nitromethyl)acrylate (3c)



3c

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.47-7.40 (m, 1H), 7.30-7.25 (m, 1H), 7.24-719 (m, 1H), 7.19-7.12 (m, 1H), 5.30 (s, 2H), 3.88 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.12; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.70, 160.24 (d, *J* = 249.5 Hz), 140.54 (d, *J* = 3.2 Hz), 132.26 (d, *J* = 8.5 Hz), 129.85 (d, *J* = 2.3 Hz), 124.79 (d, *J* = 3.7 Hz), 124.03, 121.44 (d, *J* = 14.0 Hz), 116.27 (d, *J* = 21.3 Hz), 71.82 (d, *J* = 1.8Hz), 52.84; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4F$ $[M+Na]^+$ = 262.0492, found = 262.0484.

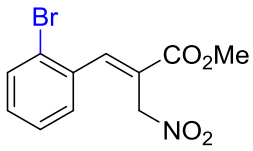
methyl (*E*)-3-(2-chlorophenyl)-2-(nitromethyl)acrylate (3d)



3d

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.47 (dd, *J* =8.0, 1.2 Hz, 1H), 7.38 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.32 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.26 (dd, *J* =7.6, 1.6 Hz, 1H), 5.23 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.63, 144.71, 134.23, 132.23, 131.25, 130.11, 129.42, 127.34, 123.86, 71.79, 52.87; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Cl$ $[M+Na]^+$ = 278.0196, found = 278.0196.

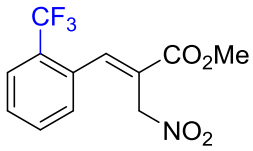
methyl (*E*)-3-(2-bromophenyl)-2-(nitromethyl)acrylate (3e)



3e

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.66 (dd, *J* =8.0, 1.2 Hz, 1H), 7.38 (ddd, *J* = 7.6, 76, 1.2 Hz, 1H), 7.30 (ddd, *J* = 7.6, 76, 1.6 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 5.22 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.61, 146.69, 134.14, 133.26, 131.31, 129.47, 127.93, 123.92, 123.58, 71.76, 52.88; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Br$ $[M+Na]^+$ = 321.9691, found = 321.9697.

methyl (*E*)-2-(nitromethyl)-3-(2-(trifluoromethyl)phenyl)acrylate (3f)

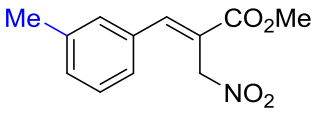


3f

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.30 (m, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.61 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.55 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 5.13 (s, 2H), 3.89 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.57; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.30, 144.33, 132.44, 132.03 (q, *J* = 1.7Hz, 129.49 (d, *J* = 43.4 Hz), 128.83 (d, *J* = 30.5 Hz), 128.02 (d, *J* = 69.8 Hz), 126.52 (q, *J* = 5.1 Hz), 124.95,

122.23, 71.48, 52.92; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}NO_4F_3$ $[M-H]^-$ = 288.0489, found = 288.0493.

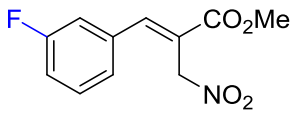
methyl (*E*)-2-(nitromethyl)-3-(m-tolyl)acrylate (3g)



3g

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.36-7.30 (m, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.15-7.08 (m, 2H), 5.36 (s, 2H), 3.87 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.28, 147.91, 138.97, 133.45, 131.01, 129.59, 129.02, 125.94, 121.74, 71.88, 52.71, 21.41; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}NO_4$ $[M+Na]^+$ = 258.0742, found = 258.0727.

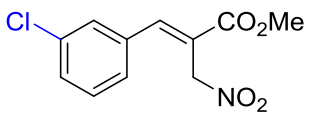
methyl (*E*)-3-(3-fluorophenyl)-2-(nitromethyl)acrylate (3h)



3h

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.42 (ddd, *J* = 8.0, 8.0 6.0 Hz, 1H), 7.17-7.08 (m, 2H), 7.06-7.01 (m, 1H), 5.33 (s, 2H), 3.87 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.07; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.83, 162.85 (d, *J* = 247.0 Hz), 146.14 (d, *J* = 2.2 Hz), 135.47 (d, *J* = 7.7 Hz), 130.90 (d, *J* = 8.3 Hz), 124.47 (d, *J* = 3.1 Hz), 123.15, 117.16 (d, *J* = 21.0 Hz), 115.78 (d, *J* = 22.2 Hz), 71.59, 52.86; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4F$ $[M+Na]^+$ = 262.0492, found = 262.0505.

methyl (*E*)-3-(3-chlorophenyl)-2-(nitromethyl)acrylate (3i)

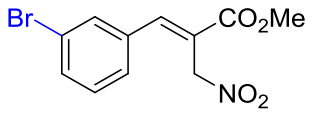


3i

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.43-7.35 (m, 2H), 7.33-7.29 (m, 1H), 7.22-7.17 (m, 1H), 5.32 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 165.79, 146.00, 135.21, 135.16, 130.46, 130.19, 128.82, 126.70, 123.28, 71.56, 52.89; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Cl$ $[M-H]^-$ = 254.0226, found = 254.0105.

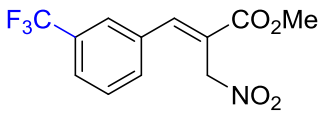
methyl (*E*)-3-(3-bromophenyl)-2-(nitromethyl)acrylate (3j)



3j

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.32 (dd, *J* = 8.0 7.6, Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 5.31 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.76, 145.87, 135.43, 133.10, 131.71, 130.66, 127.11, 123.32, 123.22, 71.53, 52.89; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Br$ $[M-H]^-$ = 297.9720, found = 297.8659.

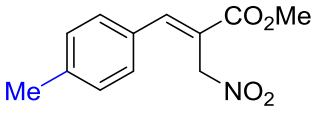
methyl (*E*)-2-(nitromethyl)-3-(3-(trifluoromethyl)phenyl)acrylate (3k)



3k

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.62-7.56 (m, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 5.30 (s, 2H), 3.89 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.66, 145.78, 134.24, 131.70 (q, *J* = 32.6 Hz), 131.63 (d, *J* = 0.9 Hz), 129.80, 126.70 (q, *J* = 3.6 Hz), 125.73(q, *J* = 3.8 Hz), 123.77, 123.54 (d, *J* = 158.9 Hz), 71.48, 52.92; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}NO_4F_3$ $[M-H]^-$ = 288.0489, found = 288.0497.

methyl (*E*)-2-(nitromethyl)-3-(p-tolyl)acrylate (3l)

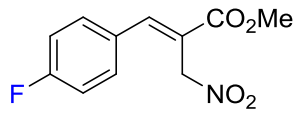


3l

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.19-7.12 (m, 4H), 5.29 (s, 2H), 3.78 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.41, 147.77,

140.83, 130.61, 129.86, 129.12, 120.98, 71.97, 52.66, 21.44; HRMS (ESI) *m/z* calcd for $C_{12}H_{13}NO_4$ $[M+Na]^+$ = 258.0742, found = 258.0730.

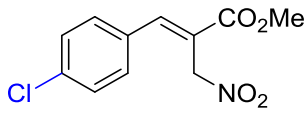
methyl (*E*)-3-(4-fluorophenyl)-2-(nitromethyl)acrylate (3m)



3m

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.37-7.30 (m, 2H), 7.18-7.11 (m, 2H), 5.34 (s, 2H), 3.87 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.01; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.08, 163.71 (d, *J* = 250.8 Hz), 146.52, 131.10 (d, *J* = 8.6 Hz), 129.56 (d, *J* = 3.4 Hz), 121.87 (d, *J* = 0.9 Hz), 116.44 (d, *J* = 21.8 Hz), 71.78, 52.80; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4F$ $[M-NO_2]^+$ = 193.0659, found = 193.0660.

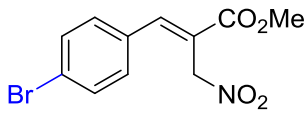
methyl (*E*)-3-(4-chlorophenyl)-2-(nitromethyl)acrylate (3n)



3n

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.47-7.39 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 3H), 5.32 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94, 146.33, 136.53, 131.83, 130.22, 129.49, 122.49, 71.69, 52.85; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Cl$ $[M-NO_2]^+$ = 209.0364, found = 209.0444.

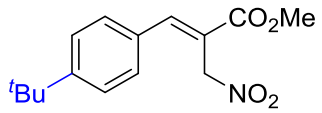
methyl (*E*)-3-(4-bromophenyl)-2-(nitromethyl)acrylate (3o)



3o

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.60-7.55 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.31 (s, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.93, 146.36, 132.44, 132.29, 130.39, 124.80, 122.57, 71.68, 52.85; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}NO_4Br$ $[M-H]^-$ = 297.9720, found = 297.9742.

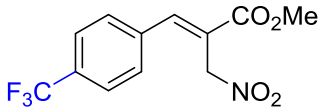
methyl (*E*)-3-(4-(tert-butyl)phenyl)-2-(nitromethyl)acrylate (3p)



3p

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.48-7.44 (m, 2H), 7.27 (d, *J* =9.2 Hz, 2H), 5.39 (s, 2H), 3.86 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.44, 153.93, 147.69, 130.59, 129.04, 126.14, 121.03, 72.00, 52.68, 34.94, 31.13; HRMS (ESI) *m/z* calcd for $C_{15}H_{19}NO_4$ $[M+Na]^+$ = 300.1212, found = 300.1201.

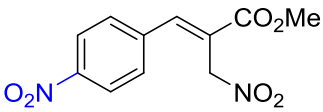
methyl (*E*)-2-(nitromethyl)-3-(4-(trifluoromethyl)phenyl)acrylate (3q)



3q

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 5.30 (s, 2H), 3.89 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.63, 145.86, 136.97 (d, *J* = 1.1 Hz), 131.88 (q, *J* = 32.7 Hz), 129.03, 126.10 (q, *J* = 3.7 Hz), 124.01, 123.62 (d, *J* = 270.7 Hz), 71.47, 52.94; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}NO_4F_3$ $[M-H]^-$ = 288.0489, found = 288.0499.

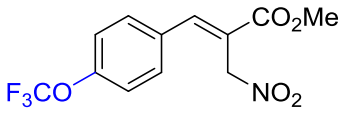
methyl (*E*)-2-(nitromethyl)-3-(4-nitrophenyl)acrylate (3r)



3r

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.20 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 5.29 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.32, 148.45, 144.86, 139.69, 129.64, 124.95, 124.31, 71.34, 53.10; HRMS (ESI) *m/z* calcd for $C_{11}H_{10}N_2O_6$ $[M-H]^-$ = 265.0466, found = 265.0490.

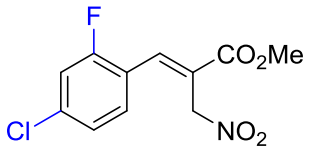
methyl (*E*)-2-(nitromethyl)-3-(4-(trifluoromethoxy)phenyl)acrylate (3s)



3s

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.40-7.35 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 2H), 3.88 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.74; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.87, 150.36 (q, *J* = 1.8 Hz), 146.01, 131.94, 130.58, 122.82, 121.38 (d, *J* =0.6 Hz), 120.34 (d, *J* =256.9 Hz), 71.64, 52.86; HRMS (ESI) *m/z* calcd for $C_{12}H_{10}NO_5F_3$ $[M-H]^-$ = 304.0438, found = 304.0435.

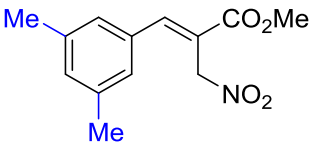
methyl (*E*)-3-(4-chloro-2-fluorophenyl)-2-(nitromethyl)acrylate (3t)



3t

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.28 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.06 (ddd, *J* = 8.0, 8.0 2.4 Hz, 1H), 5.22 (s, 2H), 3.89 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.57; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.49, 163.34 (d, *J* = 253.1 Hz), 143.69, 135.51 (d, *J* = 10.3 Hz), 130.74 (d, *J* = 9.1 Hz), 128.40 (d, *J* = 3.7 Hz), 124.02, 117.85 (d, *J* = 24.9 Hz), 114.88 (d, *J* = 21.3 Hz), 71.77, 52.94; HRMS (ESI) *m/z* calcd for $C_{11}H_9NO_4FCl$ $[M-NO_2]^-$ = 227.0275, found = 227.0270.

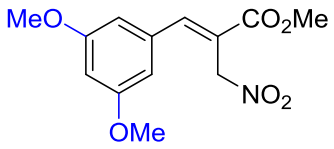
methyl (*E*)-3-(3,5-dimethylphenyl)-2-(nitromethyl)acrylate (3v)



3v

A yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.06 (s, 1H), 6.91 (s, 2H), 5.36 (s, 2H), 3.86 (s, 3H), 2.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.35, 148.10, 138.82, 133.44, 131.93, 126.65, 121.52, 71.92, 52.68, 21.29; HRMS (ESI) *m/z* calcd for $C_{13}H_{15}NO_4$ $[M+Na]^+$ = 272.0899, found = 272.0888.

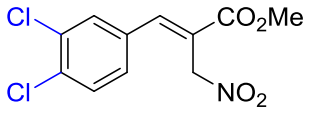
methyl (*E*)-3-(3,5-dimethoxyphenyl)-2-(nitromethyl)acrylate (3w)



3w

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 6.50 (dd, *J* = 2.4, 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 2H), 5.36 (s, 2H), 3.87 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.12, 161.19, 147.77, 135.25, 122.44, 106.58, 102.18, 71.93, 55.47, 52.75; HRMS (ESI) *m/z* calcd for $C_{13}H_{15}NO_6$ $[M+Na]^+$ = 304.0797, found = 304.0775.

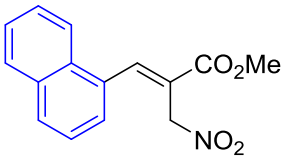
methyl (*E*)-3-(3,4-dichlorophenyl)-2-(nitromethyl)acrylate (3x)



3x

A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.17 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.30 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.60, 144.91, 134.67, 133.66, 133.26, 131.22, 130.68, 127.77, 123.60, 71.47, 52.96; HRMS (ESI) *m/z* calcd for $C_{11}H_9NO_4Cl_2$ $[M-H]^-$ = 287.9836, found = 287.8961.

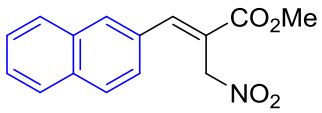
methyl (*E*)-3-(naphthalen-1-yl)-2-(nitromethyl)acrylate (3y)



3y

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.95-7.89 (m, 2H), 7.88-7.83 (m, 1H), 7.60-7.54 (m, 2H), 7.49 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 5.27 (s, 2H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.87, 146.51, 133.47, 131.20, 130.80, 130.47, 128.78, 127.21, 126.81, 126.16, 125.38, 124.26, 124.20, 72.03, 52.82; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}NO_4$ $[M+Na]^+$ = 294.0742, found = 294.0713.

methyl (*E*)-3-(naphthalen-2-yl)-2-(nitromethyl)acrylate (3z)

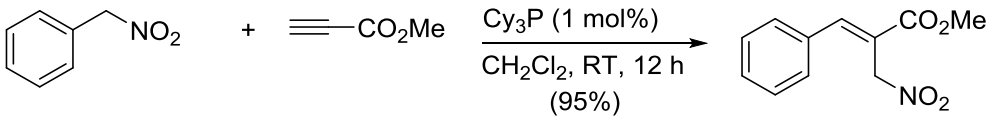


3z

A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.92-7.81 (m, 4H), 7.60-7.52 (m, 2H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.44 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.28, 147.80, 133.71, 133.00, 130.90, 129.26, 129.01, 128.61, 127.81, 127.73, 127.10, 125.58, 121.99, 72.04, 52; HRMS (ESI) *m/z* calcd for $C_{15}H_{13}NO_4$ $[M+Na]^+$ = 294.0742, found = 294.0743.

5. Procedure for the Gram-scale Synthesis and Elaborations

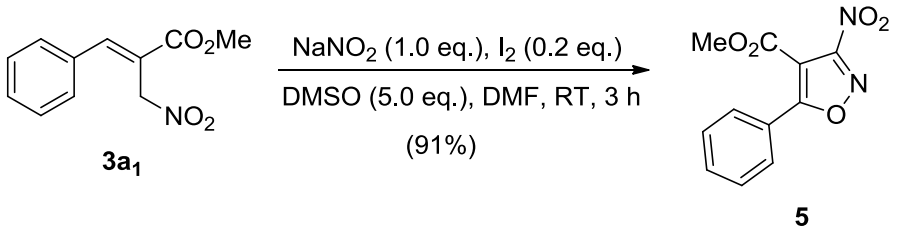
A. Gram-scale Synthesis



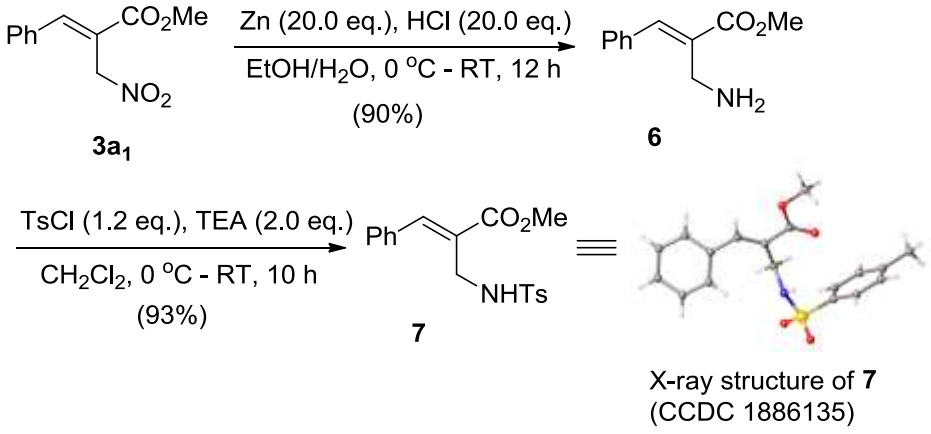
1a **2a** **3a$_1$**

To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene **1a** (1.371 g, 10 mmol), Cy_3P (28.0 mg, 0.1 mmol), and followed by the addition of dry CH_2Cl_2 (70 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate **2a** (1.261 g, 15 mmol) in CH_2Cl_2 (10 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for overnight, and TLC show that the reaction was completed. Then the CH_2Cl_2 was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford **3a$_1$** (2.100 g, 95% yield) as a yellow oil.

B. Elaborations of product



To a stirred solution of **3a$_1$** (66.4 mg, 0.3 mmol) in DMF (3.0 mL) was added $NaNO_2$ (20.7 mg, 0.3 mmol) at room temperature in open air. I_2 (15.2 mg, 0.06 mmol) and DMSO (110 µL, 1.5 mmol) were added to the reaction mixture at the same temperature and the reaction was allowed to continue for 3 h. There after the reaction was quenched by the addition of $Na_2S_2O_3$ (10% w/w aqueous, 4.2 mL) and the resulting mixture was extracted with ethyl acetate (3 x 10 mL). The combined organic fractions were dried over Na_2SO_4, and the solvent was removed under vacuum. The crude product thus obtained was purified chromatography over a column of silica gel using hexane/ ethyl acetate (20:1) as eluent to afford the desired product **5** (67.5 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.99 (m, 2H), 8.02-8.00 (m, 1H), 7.66-7.60 (m, 1H), 7.59-7.53 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.32, 159.15, 132.99, 129.08, 128.67, 124.85, 102.96, 53.26; HRMS (ESI) *m/z* calcd for $C_{11}H_8N_2O_5$ $[M+NH_4]^+$ = 266.0771, found = 266.0490.



The compound **6** was prepared using a modified procedure by Trost et al.[2], **3a$_1$** (664 mg, 3.0 mmol) was taken in HCl/EtOH/H_2O (27.5 mL, 3.0 M, 60.0 mmol, EtOH/H_2O = 1:2) and Zn powder (3.923 g, 60.0 mmol) was introduced to the solution

portionwise. The mixture was stirred for 12 h at ambient temperature. The reaction mixture was diluted with water and the aqueous phase was extracted with ethyl acetate twice. The combined organic extracts were washed with brine and dried over Na_2SO_4. After concentration, the resulting residue was purified by column chromatography on silica gel (eluting with 1:1 hexane/ethyl acetate unless otherwise stated) to afford the corresponding amine **6** in 90% yield (516 mg, 2.7 mmol).

To a solution of amine **6** (310 mg, 1.6 mmol) and Et_3N (0.44 mL, 3.2 mmol) anhydrous CH_2Cl_2 (15.0 mL) was slowly added a solution of p-toluenesulfonyl chloride (366 mg, 1.92 mmol) at 0 ^oC. The resulting mixture was warmed to room temperature and stirred for 10 h. Water was added and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers was washed with brine and dried over Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified column chromatography on silica gel using hexane/ethyl acetate (15:1) as an eluent to afford **7** (514 mg, 93% yield) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.70-7.64 (m, 2H), 7.38 (s, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.32 (s, 1H), 3.94 (d, *J* = 6.4 Hz, 2H), 3.74 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.68, 143.52, 143.47, 136.50, 133.92, 129.66, 129.53, 128.77, 127.28, 126.48, 52.32, 40.53, 21.54.

The single crystal confirmed the structure of compound **7**, and CCDC **1886135** contains the supplementary crystallographic data which can be obtained free of charge from The Cambrige Crystallographic Data Centere via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S5 **Crystal data and structure refinement for wtl-hgf-r1.**

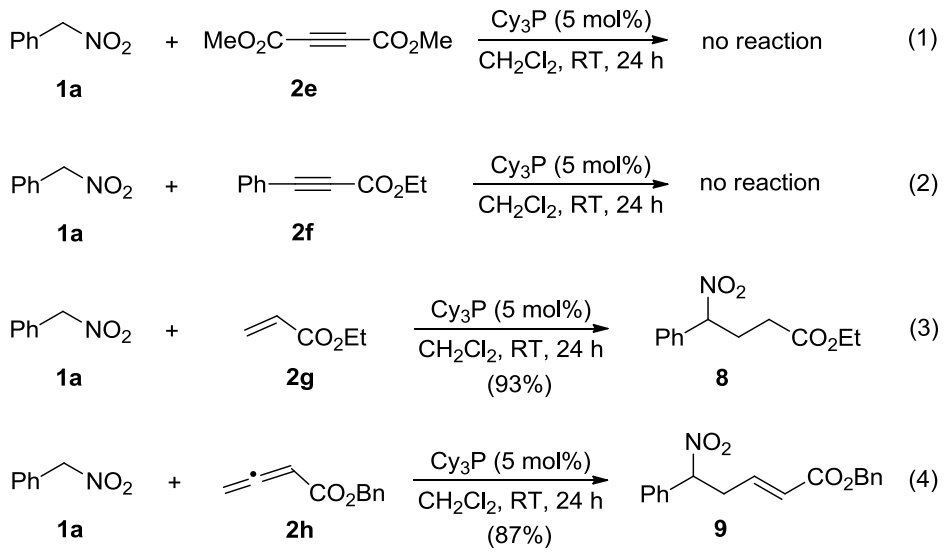
Identification code	wtl-hgf-r1
Empirical formula	$C_{18}H_{19}NO_4S$
Formula weight	345.40
Temperature/K	296.8(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	17.4772(6)
b/Å	10.4880(5)

c/Å	19.6463(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	3601.2(2)
Z	8
$\rho_{calc}g/cm^3$	1.274
μ/mm^{-1}	1.775
F(000)	1456.0
Crystal size/mm^3	0.6 ×0.5 ×0.4
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.002 to 145.962
Index ranges	$-13 \leq h \leq 21$, $-12 \leq k \leq 8$, $-24 \leq l \leq 24$
Reflections collected	13783
Independent reflections	3508 [R_{int} = 0.0304, R_{sigma} = 0.0190]
Data/restraints/parameters	3508/0/222
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1592
Final R indexes [all data]	R_1 = 0.0659, wR_2 = 0.1727
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.39

6. Mechanism Studies

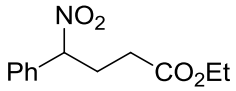
A. Control experiments

In this study, we preformed further experiments to gain a better understanding of our reaction. A few common electrophiles were examined in their reactions with phenyl nitromethane **1a** (Scheme S2). When alkyne **2e** and **2f** were used as acceptors, the reactions could not be initiated and turned out to be no reaction. On the contrary, once alkyne was changed to alkene or allene, the rearrangement didn't take place and only additive products were observed. These results imply that terminal alkynes are crucial for the reactivity as well as rearrangement process.



Scheme S2. Control experiments

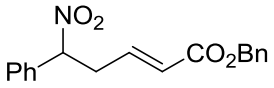
ethyl 4-nitro-4-phenylbutanoate (8)



8

A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.43 (m, 2H), 7.43-7.38 (m, 3H), 5.58 (dd, *J* = 6.8, 6.4 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.82-2.71 (m, 1H), 2.49-2.38 (m, 1H), 2.35 (dd, *J* = 6.8, 7.2 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.83, 134.01, 130.04, 129.16, 127.68, 90.07 (d, *J* = 1.4 Hz), 60.90, 30.34, 28.91, 14.17.

benzyl (E)-5-nitro-5-phenylpent-2-enoate (9)



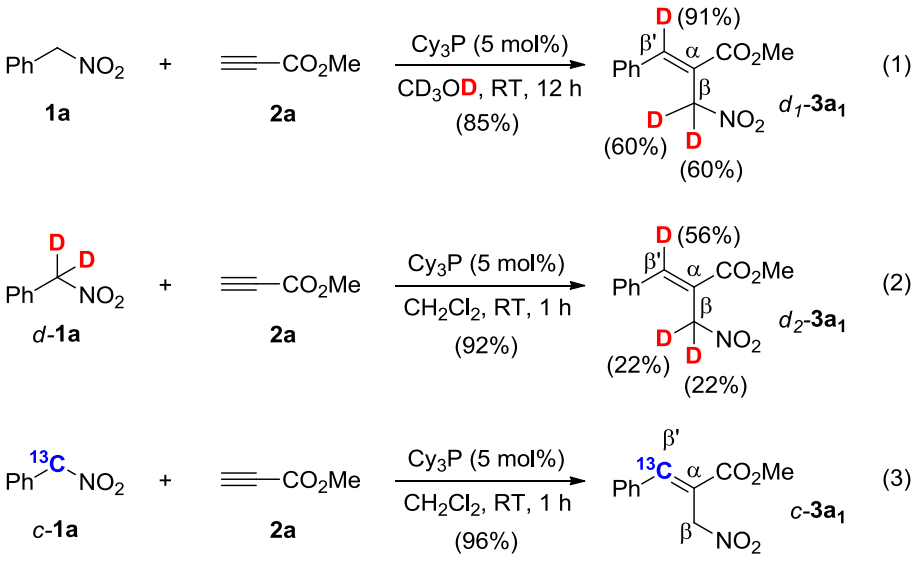
9

A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.41 (m, 5H), 7.38-7.32 (m, 5H), 6.87-6.78 (m, 1H), 6.00 (ddd, *J* = 15.6, 1.6, 1.2 Hz, 1H), 5.54 (dd, *J* = 8.8, 6.0 Hz, 1H), 5.16 (s, 2H), 3.44-334 (m, 1H), 3.02-2.93 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)

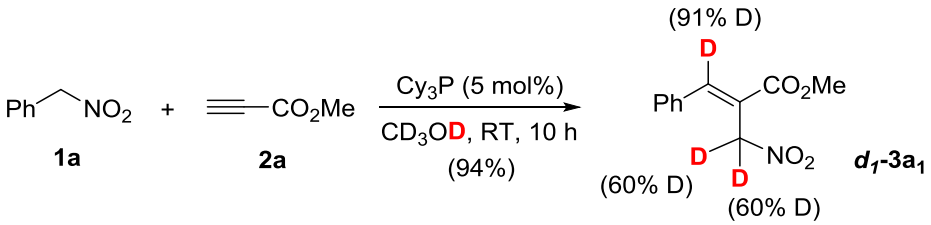
δ 165.35, 141.21, 135.70, 133.45, 130.30, 129.28, 128.61, 128.35, 128.30, 127.59, 125.29, 89.34 (d, *J* = 1.8 Hz), 66.47, 36.09.

B. Isotope labelling experiments

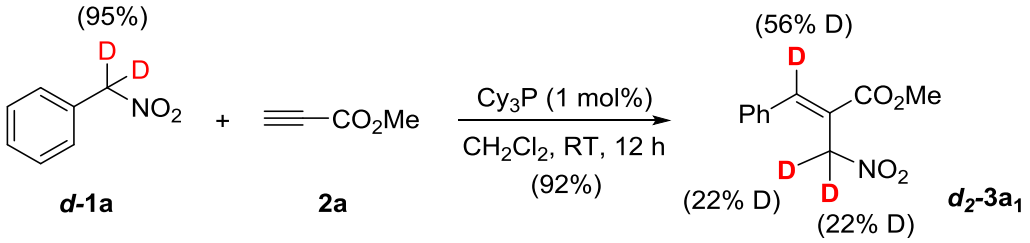
Next, isotope labelling experiments were also performed for gaining further understanding of the reaction mechanism, and the results were shown in Scheme S3. When reaction between 1a and 2a was conducted in the solvent of deuterated methanol, deuterium incorporation into both β-position (60% of D) and β'-position (91% of D) of the Tandem product was observed (eq. 1). When the deuterium-labelling substrate ***d*-1a** was used, we also obtained the similar product with containing D-atom at both β- and β'-positions in high yield (eq. 2). Notably, the reaction of ^{13}C-labeled phenyl-nitromethane ***c*-1a** and methyl propiolate **2a** afforded the corresponding Tandem product ***c*-3a$_1$** with only incorporating ^{13}C-atom at its β'-position (eq. 3 and Figure S2). These results demonstrated the desired product**s** was constructed via a α-umpolung/1,3-rearrangement sequence.



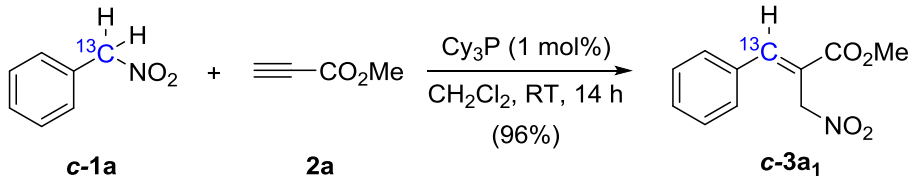
Scheme S3. Isotope labelling experiments.



To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl)benzene **1a** (27.4 mg, 0.2 mmol) and Cy_3P (2.8 mg, 0.01 mmol), followed by the addition of CD_3OD (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate **2a** (25.2 mg, 0.3 mmol) in CD_3OD (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 10 h, and TLC show that the reaction was completed. Then, the CD_3OD was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford ***d*$_1$-3a$_1$** (41.6 mg, 94% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 0.09H), 7.46-7.42 (m, 3H), 7.35-7.30 (m, 2H), 5.37-5.33 (m, 0.81H), 3.87 (s, 3H).



To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl-d_2)benzene ***d*-1a** (27.8 mg, 0.2 mmol) and Cy_3P (0.6 mg, 0.002 mmol), followed by the addition of CH_2Cl_2 (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate **2a** (25.2 mg, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH_2Cl_2 was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford ***d*$_2$-3a$_1$** (41.0 mg, 92%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.46-7.40 (m, 3H), 7.35-7.29 (m, 2H), 5.36-5.33 (m, 2H), 3.87 (s, 3H).



***c*-1a** **2a** ***c*-3a$_1$**

To a flame-dried round bottle flask with a magnetic stirring bar were added (nitromethyl-^{13}C)benzene ***c*-1a** (27.6 mg, 0.2 mmol) and Cy_3P (0.6 mg, 0.002 mmol), followed by the addition of CH_2Cl_2 (1.5 mL). The above mixture was stirred at room temperature, and then a solution of the methyl propiolate **2a** (25.2 mg, 0.3 mmol) in CH_2Cl_2 (0.5 mL) was slowly added via syringe under inert atmosphere. The reaction mixture was stirred at room temperature for 12 h, and TLC show that the reaction was completed. Then, the CH_2Cl_2 was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20:1) to afford ***c*-3a$_1$** (42.5 mg, 96% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 158.8 Hz, 1H), 7.48-7.41 (m, 3H), 7.36-7.28 (m, 2H), 5.35 (d, *J* = 4.0 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.22 (d, *J* = 1.7 Hz), 147.70, 133.55 (dd, *J* = 141.6, 104.2 Hz), 130.22, 129.14 (d, *J* = 4.2 Hz), 128.92 (d, *J* = 2.2 Hz), 121.92 (d, *J* = 73.2 Hz), 71.84, 52.77; HRMS (ESI) *m/z* calcd for $C_{10}{}^{13}CH_{11}NO_4$ $[M+Na]^+$ = 245.0619, found = 245.0583.

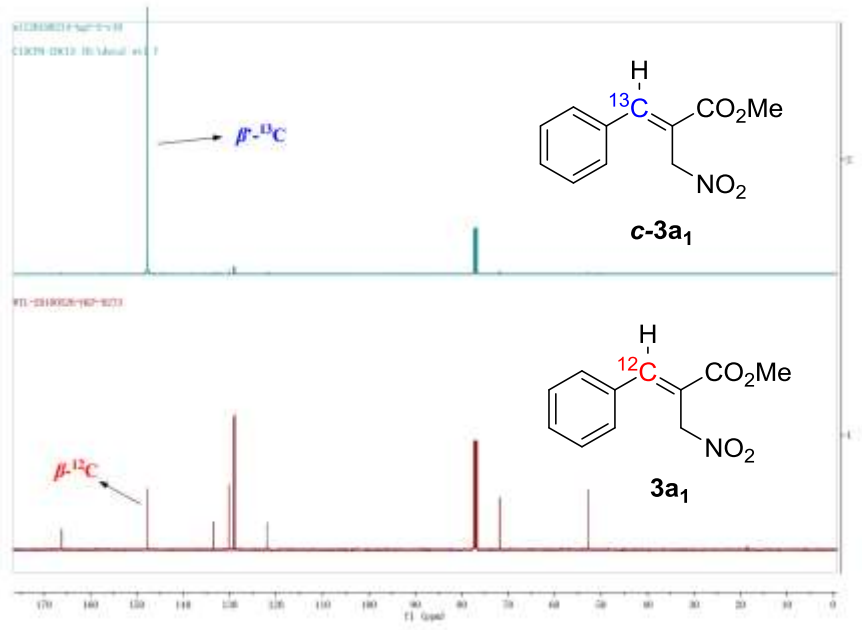
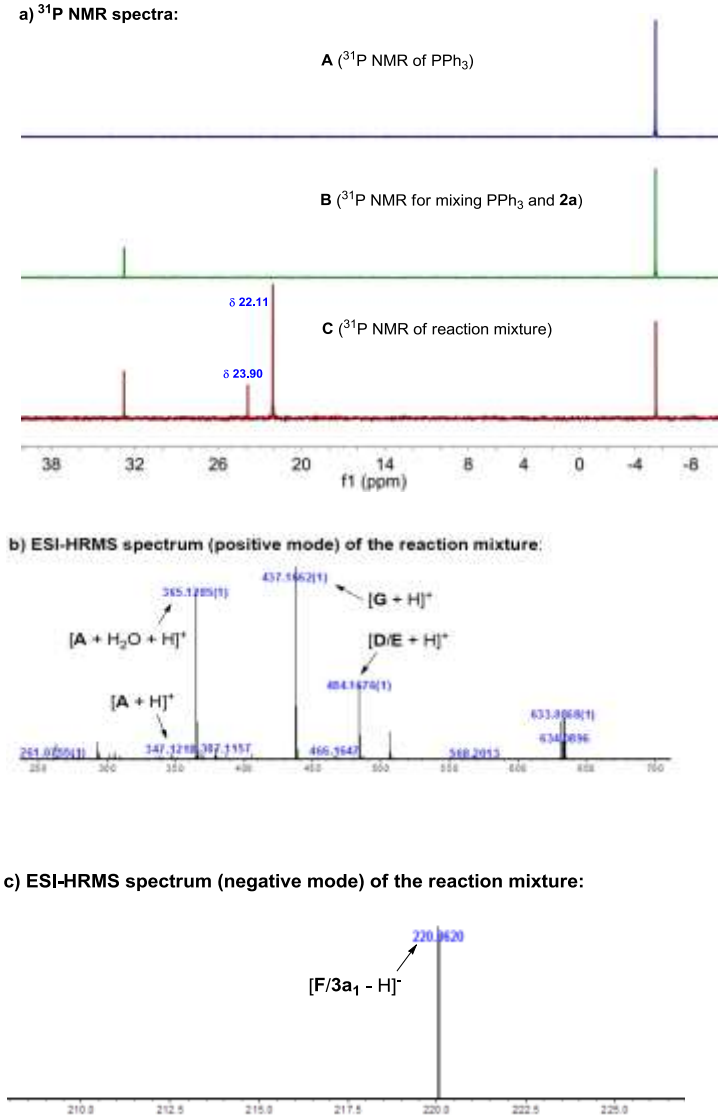


Figure S2. ^{13}C NMR spectra of the products **3a$_1$** and *c*-**3a$_1$**.

C. In situ ^{31}P NMR and ESI-HRMS studies



Scheme S4. ^{31}P NMR and ESI-HRMS spectra for characterization of reaction intermediates.

To gain further insight of the reaction mechanism, we then employed ^{31}P NMR and ESI-MS techniques for characterization of this catalytic system (Scheme S4). Accordingly, the room-temperature ^{31}P NMR spectra of reaction mixtures were taken, respectively. As compared with the spectra of catalyst PPh_3 (δ -5.45 ppm, spectrum A) and intermediate A (δ 32.80 ppm, spectrum B) generated from mixing the PPh_3 and alkyne **2a**, the ^{31}P NMR spectrum of the reaction mixture after stirring 25 minutes (spectrum C) exhibited some characteristic phosphorus signals for the possible reaction intermediates; for

instance, the well-resolved phosphorus signals at δ 22.11 and 23.90 ppm suggested the existence of the intermediate **G** and possible **D**/**E** in the reaction mixture. Furthermore, the ESI-HRMS spectrum of this reaction mixture was also collected in positive-ion mode and shown the existence of this intermediate **G** (Scheme S4b).

D. Proposed reaction cycle

According to the preliminary mechanism studies, we proposed the reaction mechanism for this Tandem reaction. As shown in Figure S3, the first conjugate addition of phosphine to electron-deficient alkyne **2a** generates zwitterion **A**, which deprotonates the incoming nucleophile **1a**, resulting in the formation of an ion pair that consists of the cationic form of the phosphonium intermediate **B** and nucleophile **C**. The next α-selective addition of **C** to the intermediate **B** leads to intermediate **D,** and then 1,2-proton shift to give **E.** Subsequently, β-elimination of the phosphine catalyst may occur to generate the α-umpolung adduct **F**. Under the phosohine catalytic conditions, 1,3-rearrangement process of the nitro group take**s** place via allyl phosphonium intermediate **G** to afford the final Tandem product **3a$_1$** and complete the catalytic cycle.

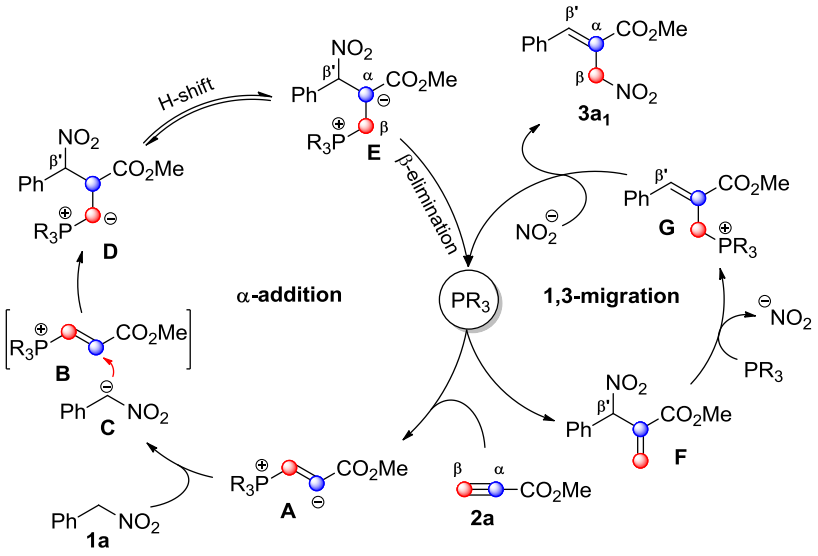


Figure S3. Plausible mechanism.

7. References

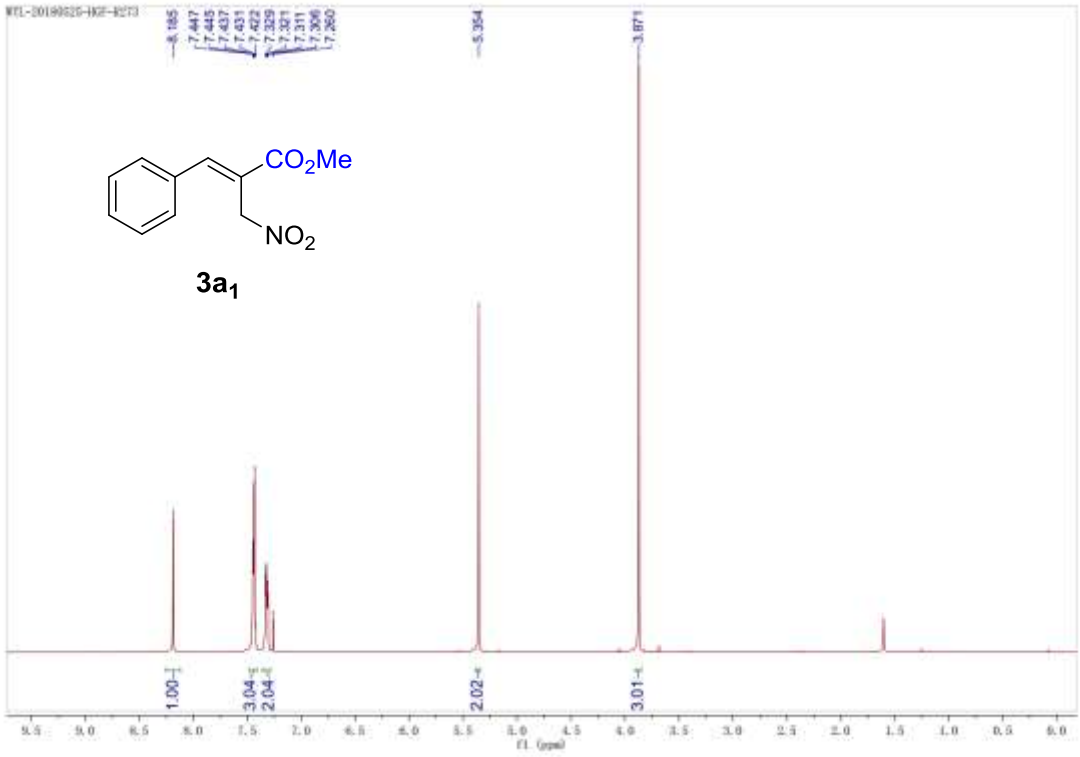
[1] P. Marcé, J. Lynch, A. J. Blackerb and J. M. J. Williams, *Chem. Commun.*, 2016, **52**, 1013;

[2] B. M. Trost, V. Ehmke, B. M. O'Keefe, and D. A. Bringley, *J. Am. Chem. Soc*., 2014, **136**, 8213;

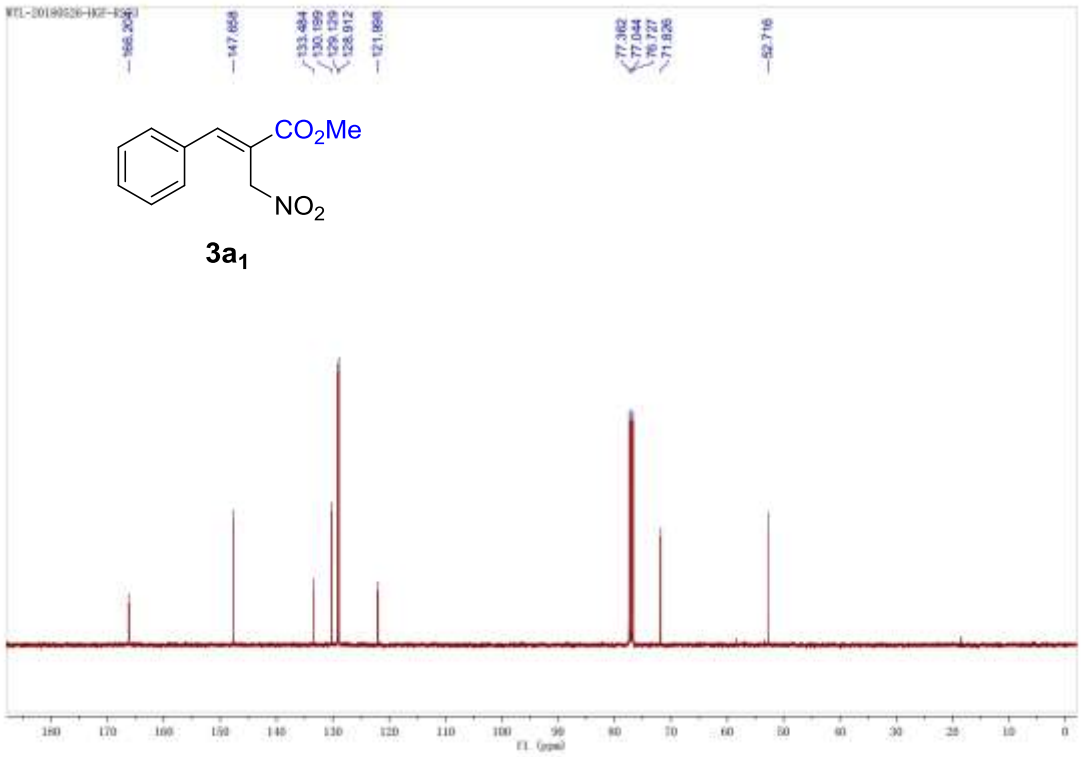
[3] G. Yin, Y. Wu, and G. Liu, *J. Am. Chem. Soc*., 2010, **132**, 11978;

[4] B. Lipp, A. Lipp, H. Detert and T. Opatz, *Org. Lett*., 2017, **19**, 2054.

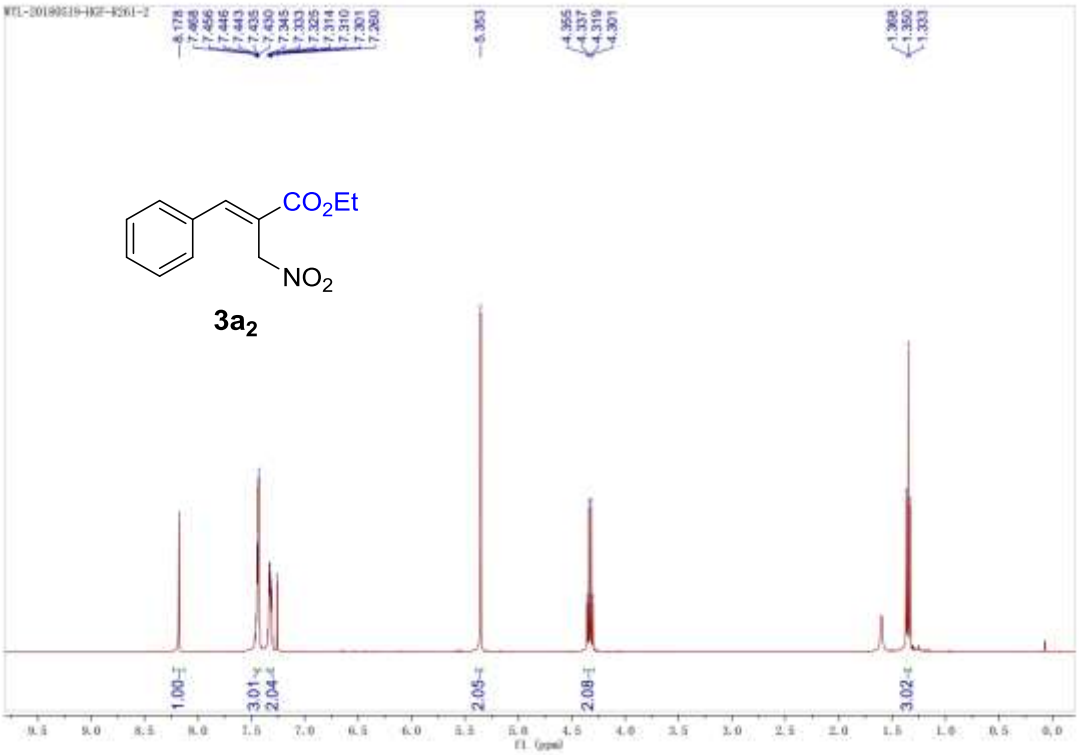
8. NMR Spectra of the Products

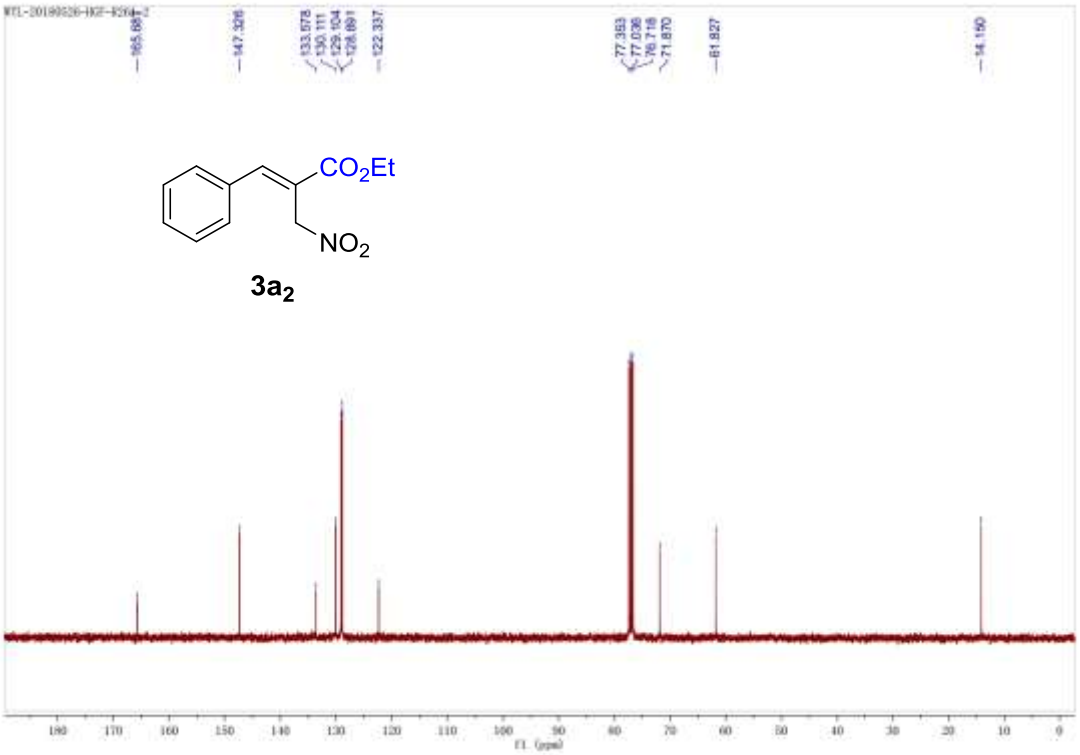


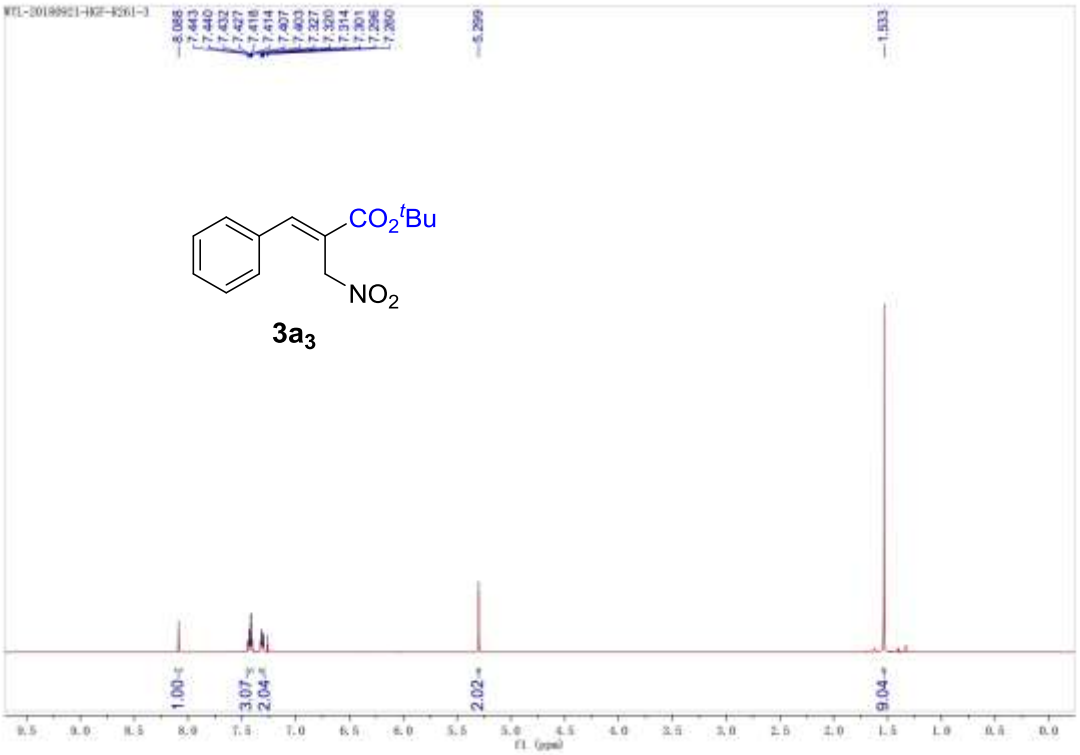
3a1



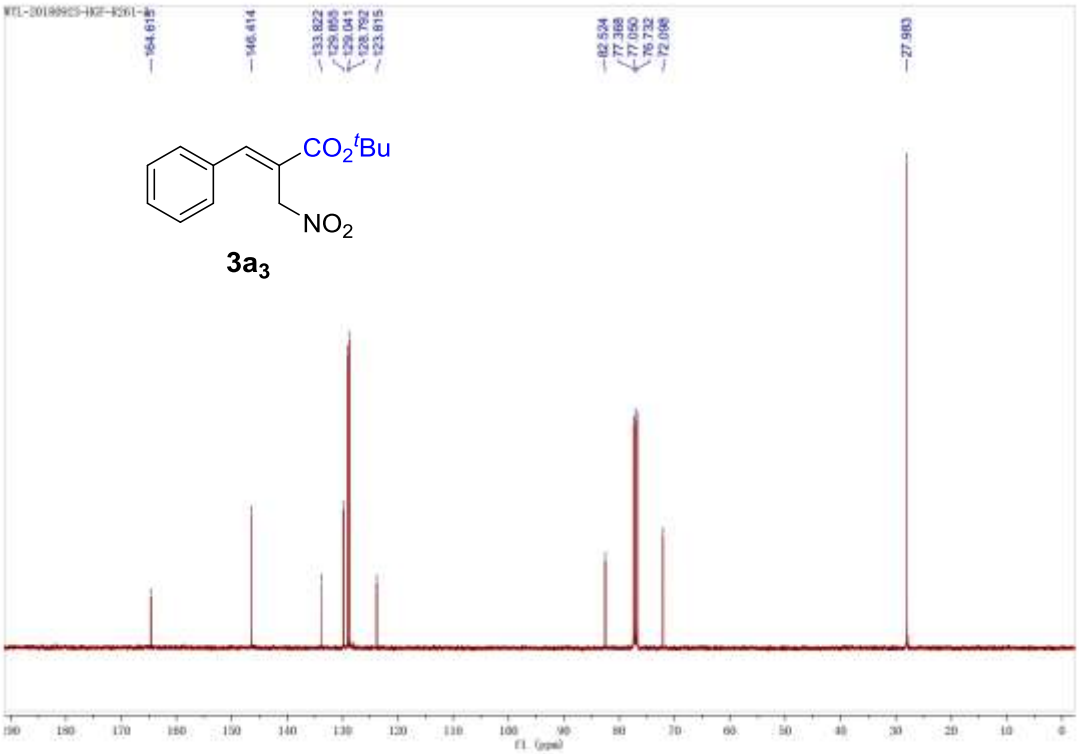
3a1


CO2Et
NO2
3a2

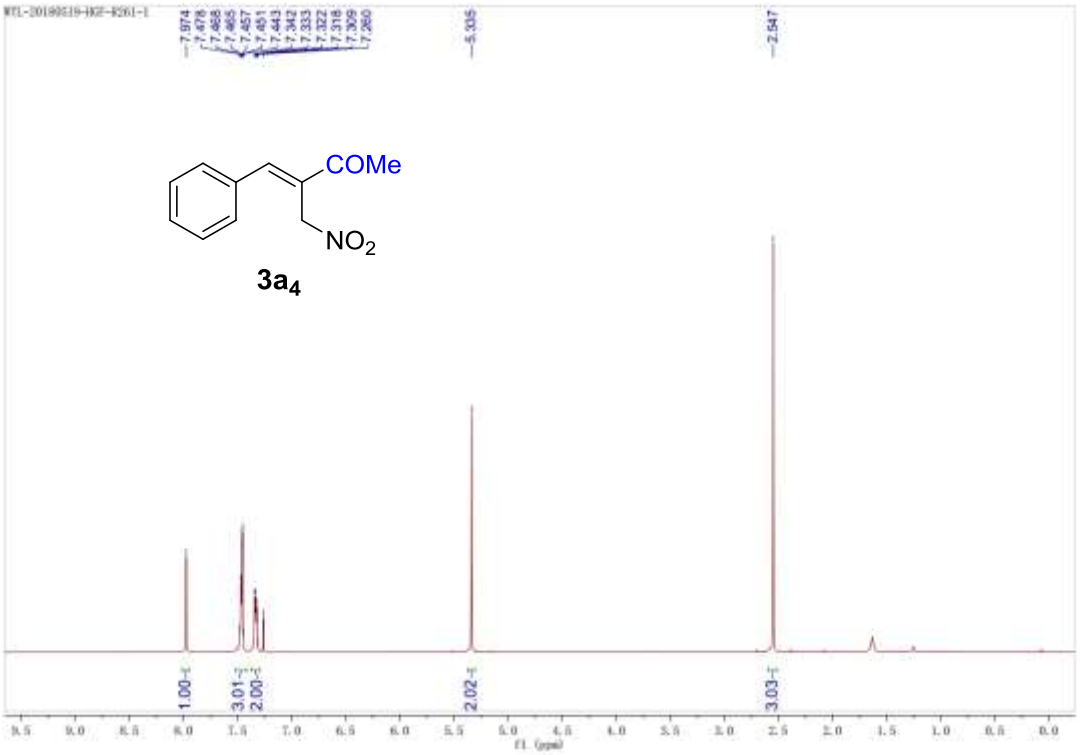

CO2Et
NO2
3a2

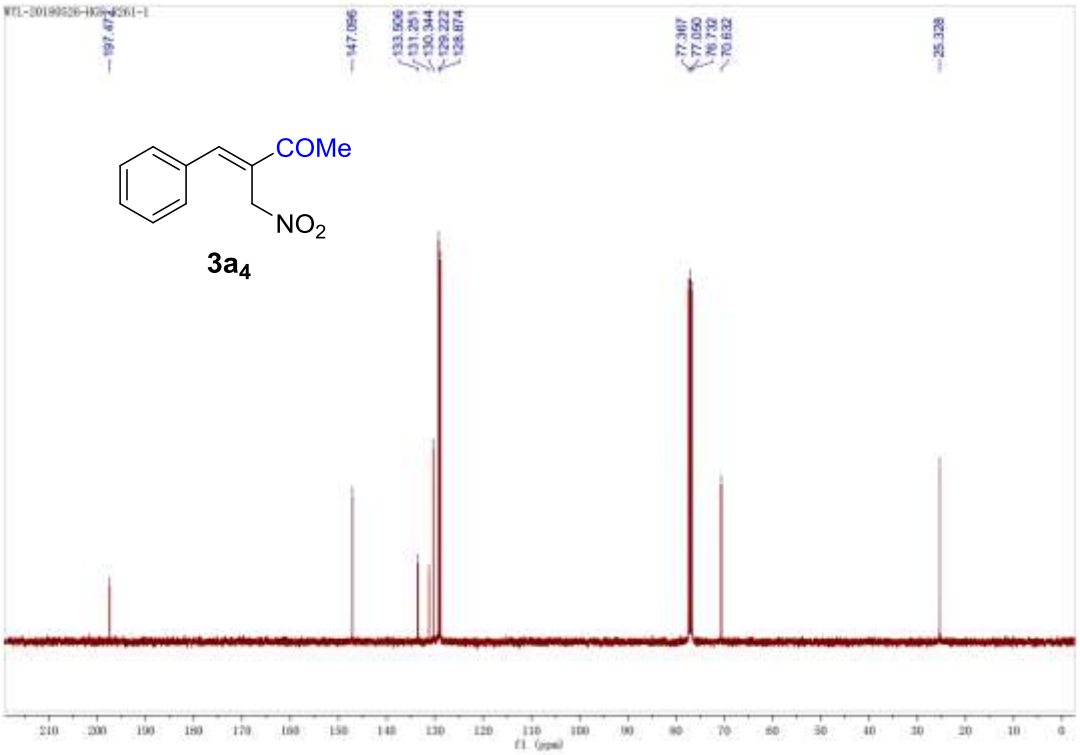

8.088
7.443
7.440
7.432
7.427
7.418
7.414
7.407
7.403
7.327
7.320
7.314
7.301
7.296
7.280
5.299
1.533
CO2tBu
NO2
1.00
3.07
2.04
2.02
9.04

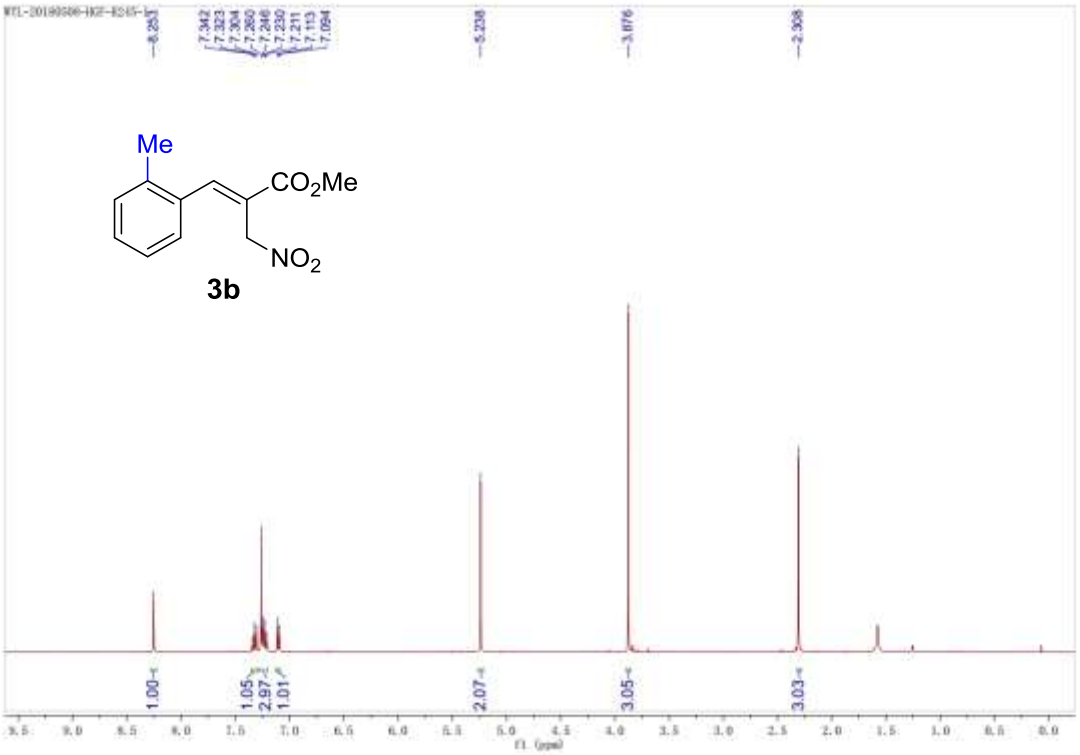
3a$_3$

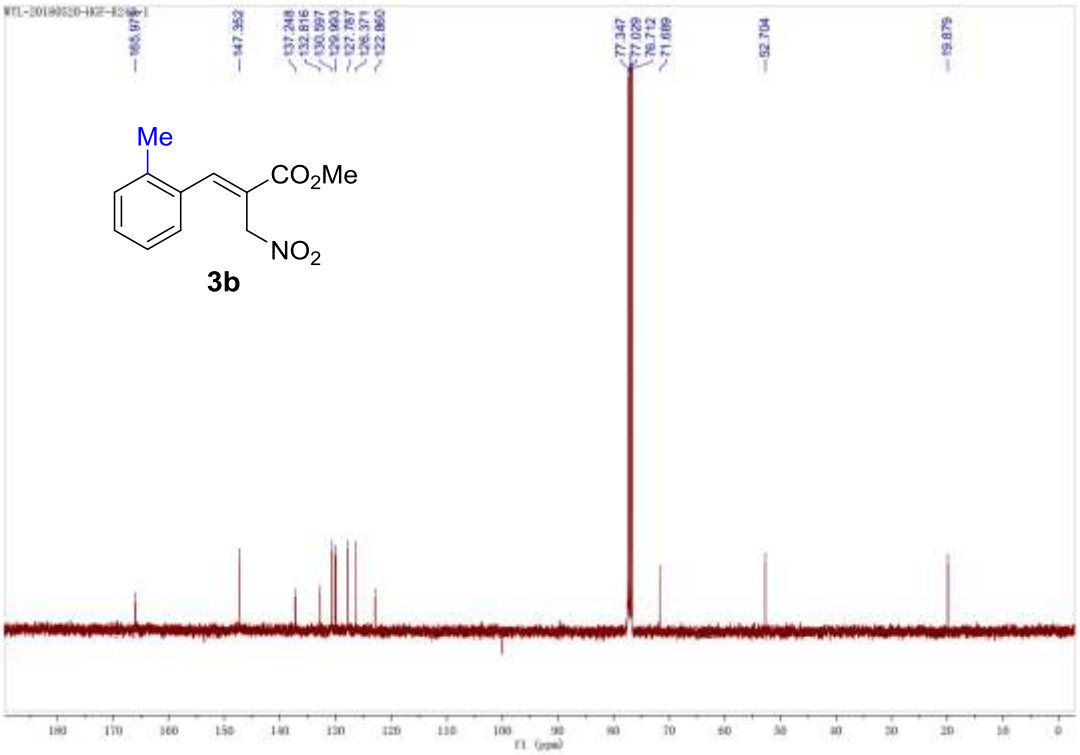

164.618
146.414
133.822
129.858
129.041
128.752
123.815
82.524
77.368
77.050
76.732
72.098
27.983
CO2tBu
NO2

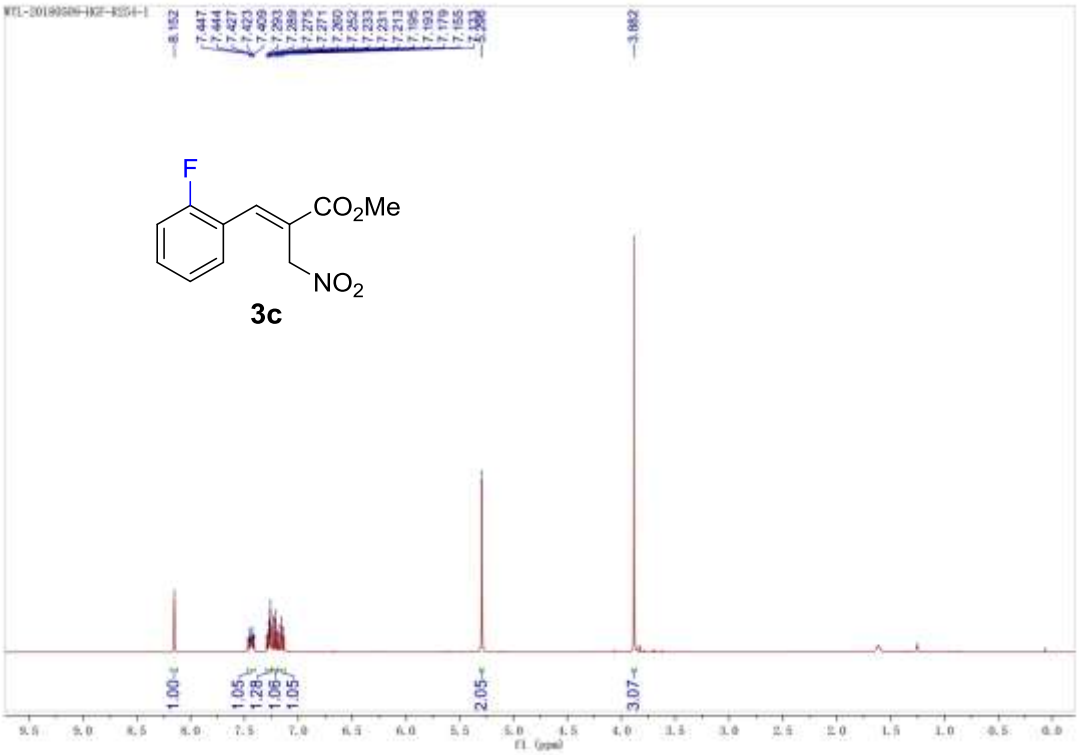
3a$_3$

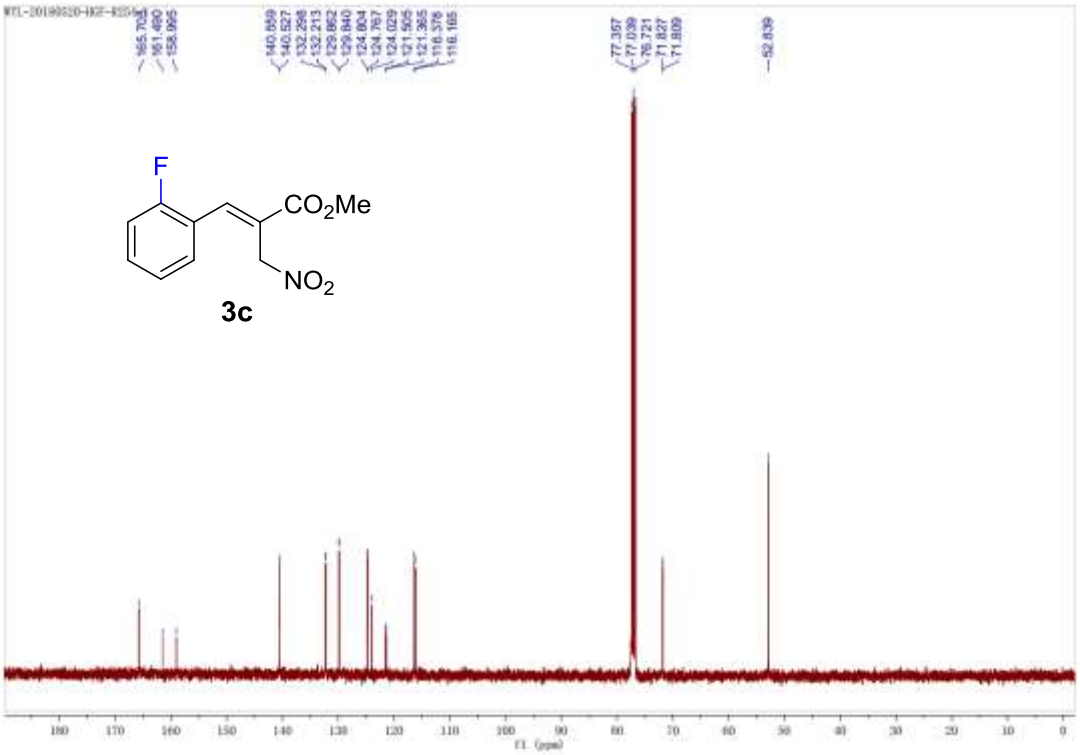

COMe
NO2
3a4

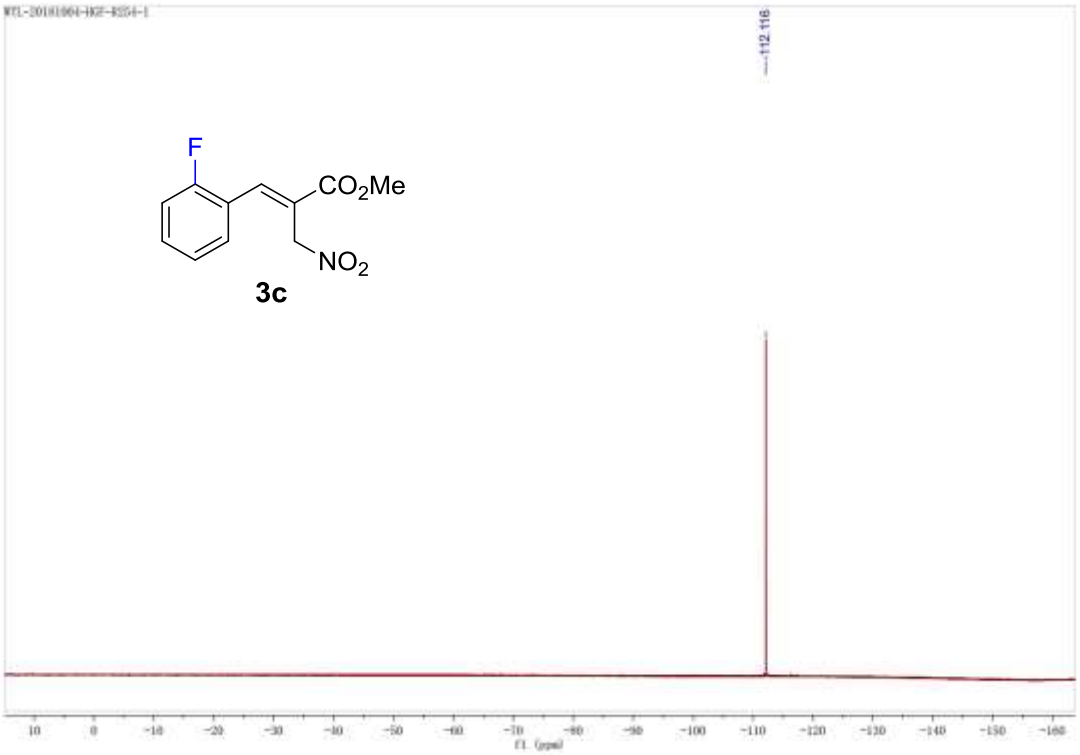

COMe
NO2
3a4

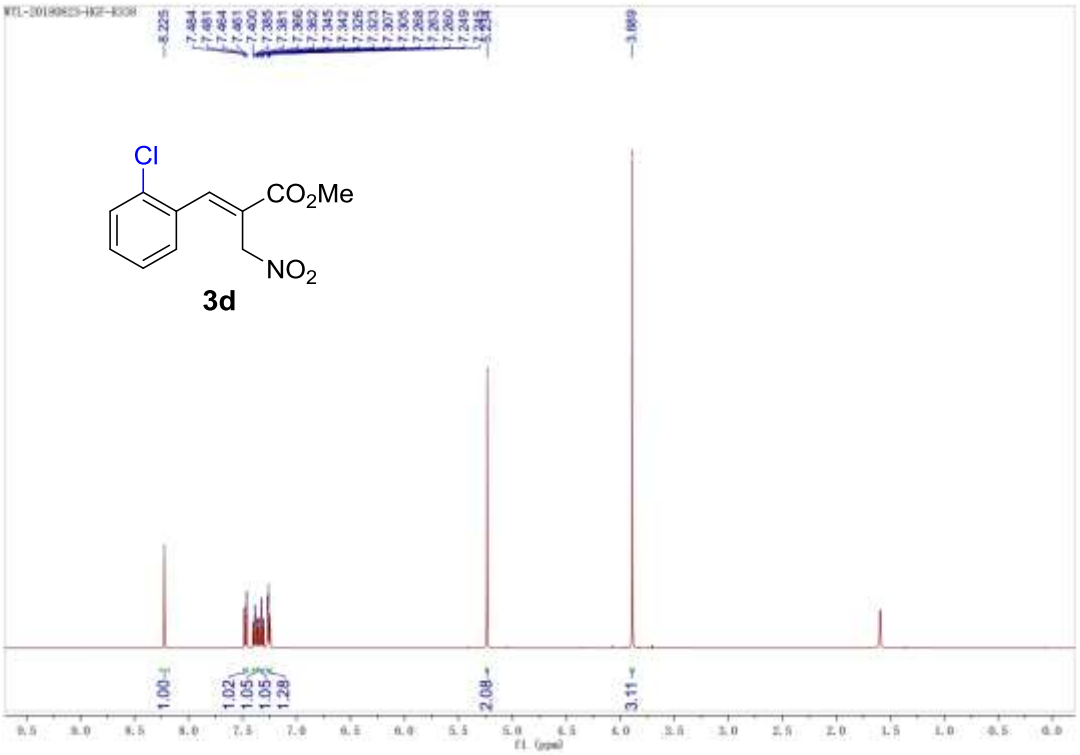

Me
CO2Me
NO2
3b

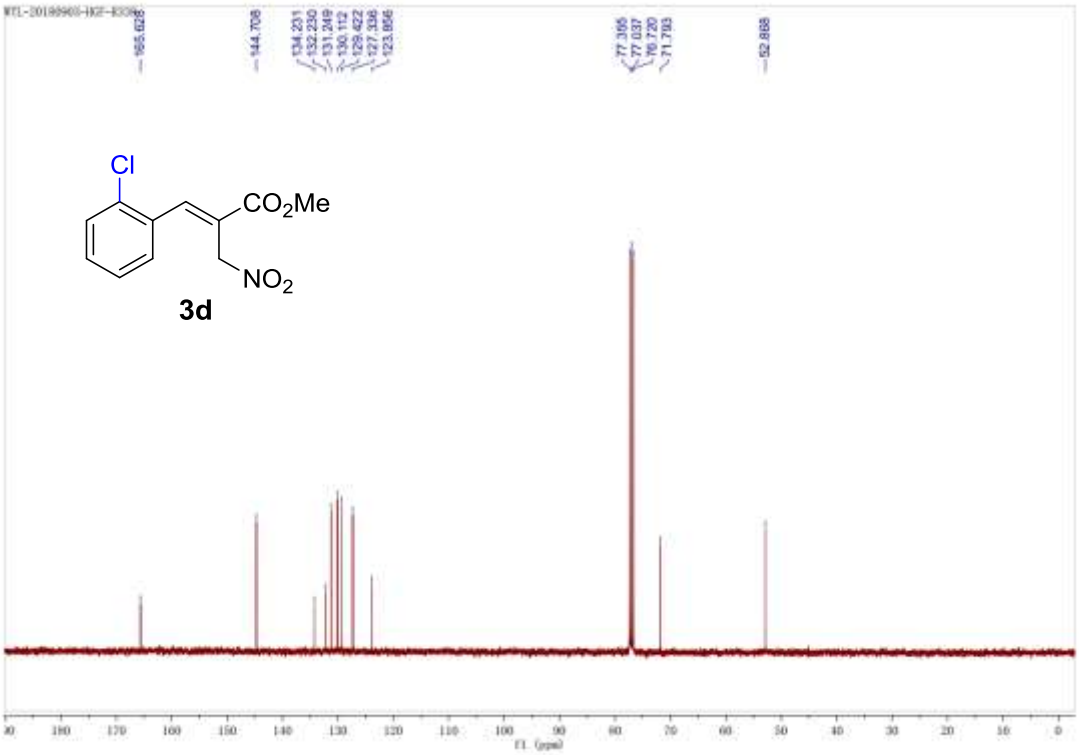

Me
CO2Me
NO2
3b

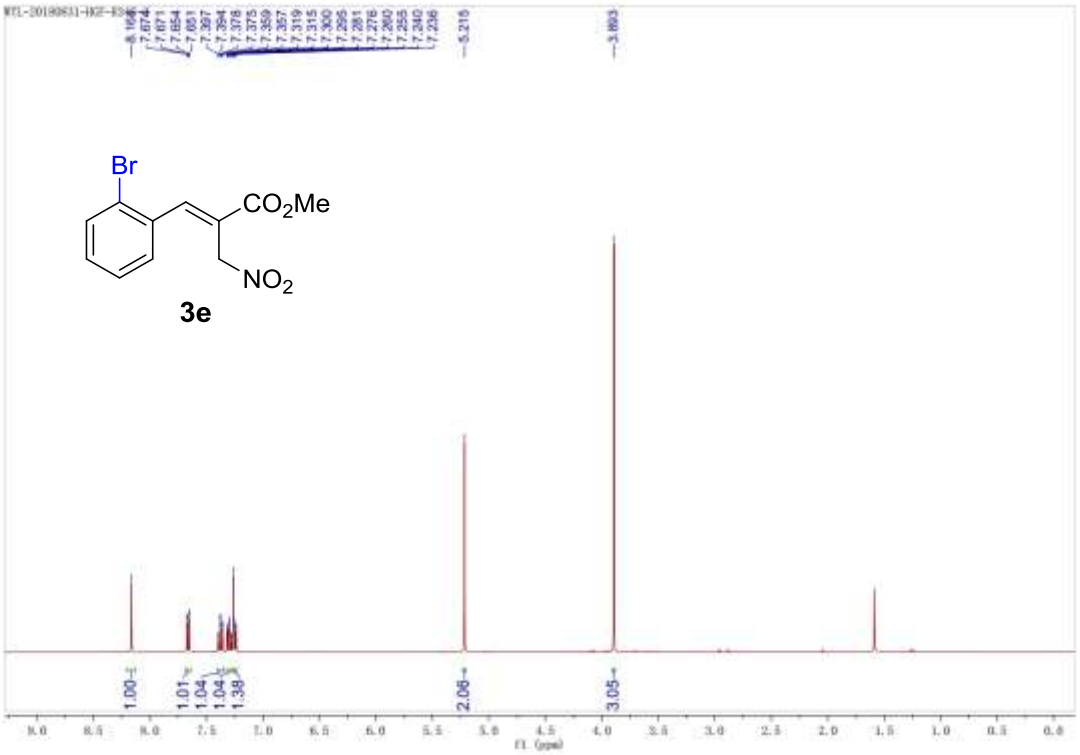

F
CO2Me
NO2
3c

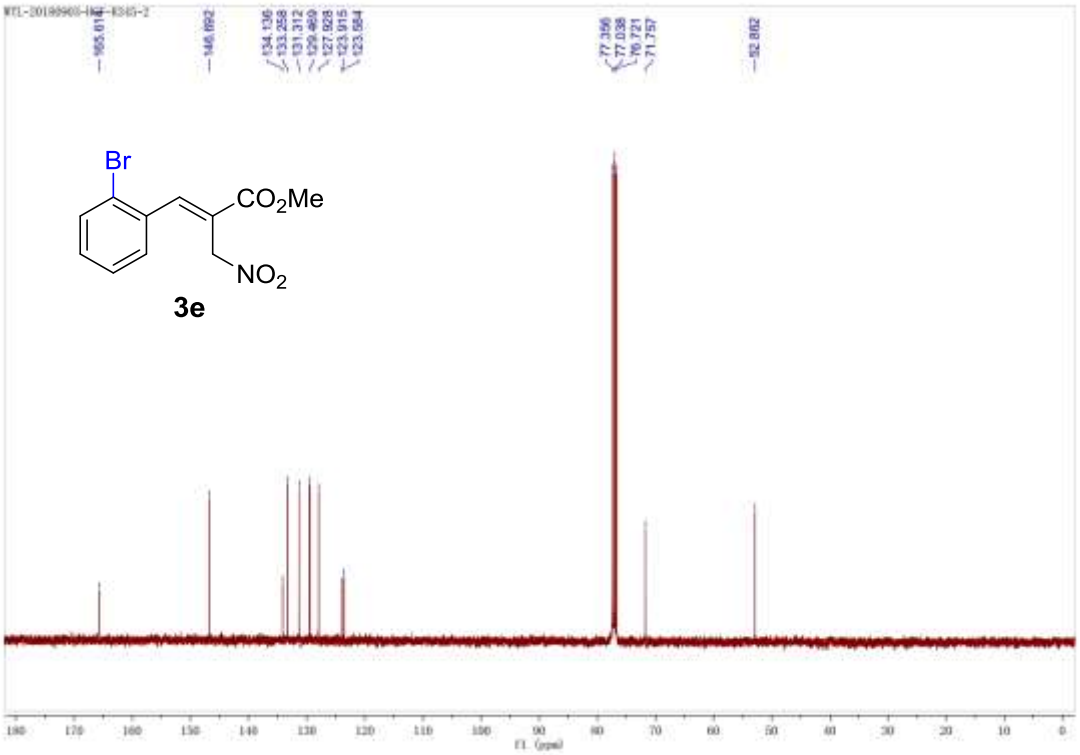

F
CO2Me
NO2
3c

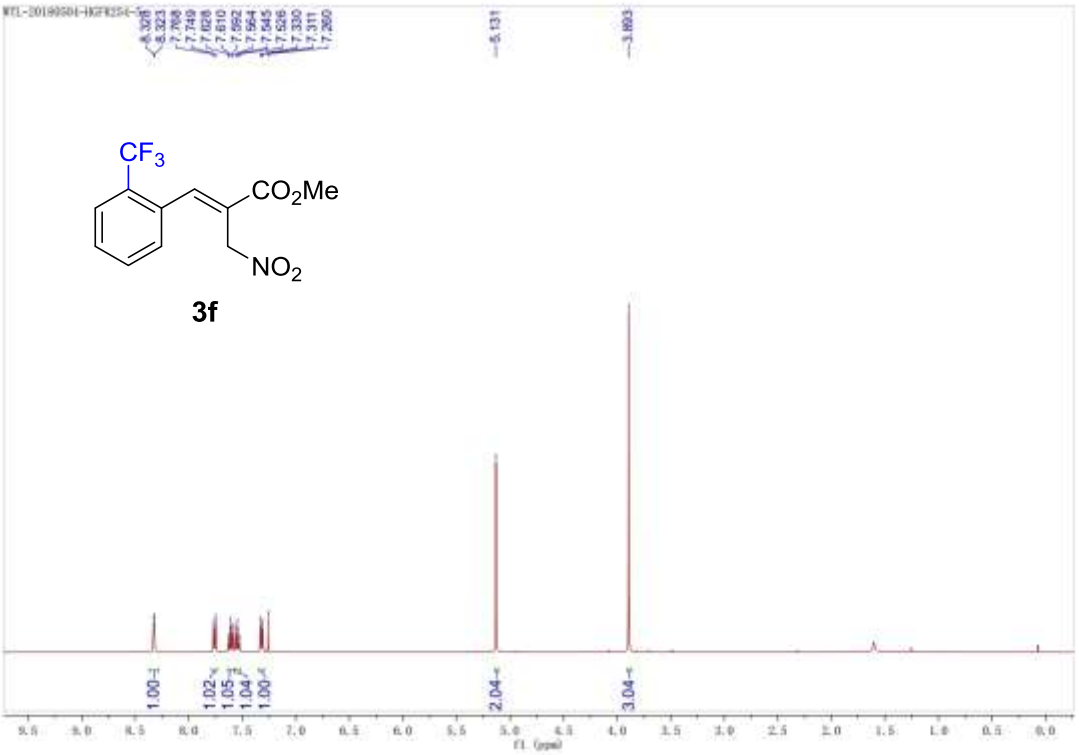

F
CO2Me
NO2
3c

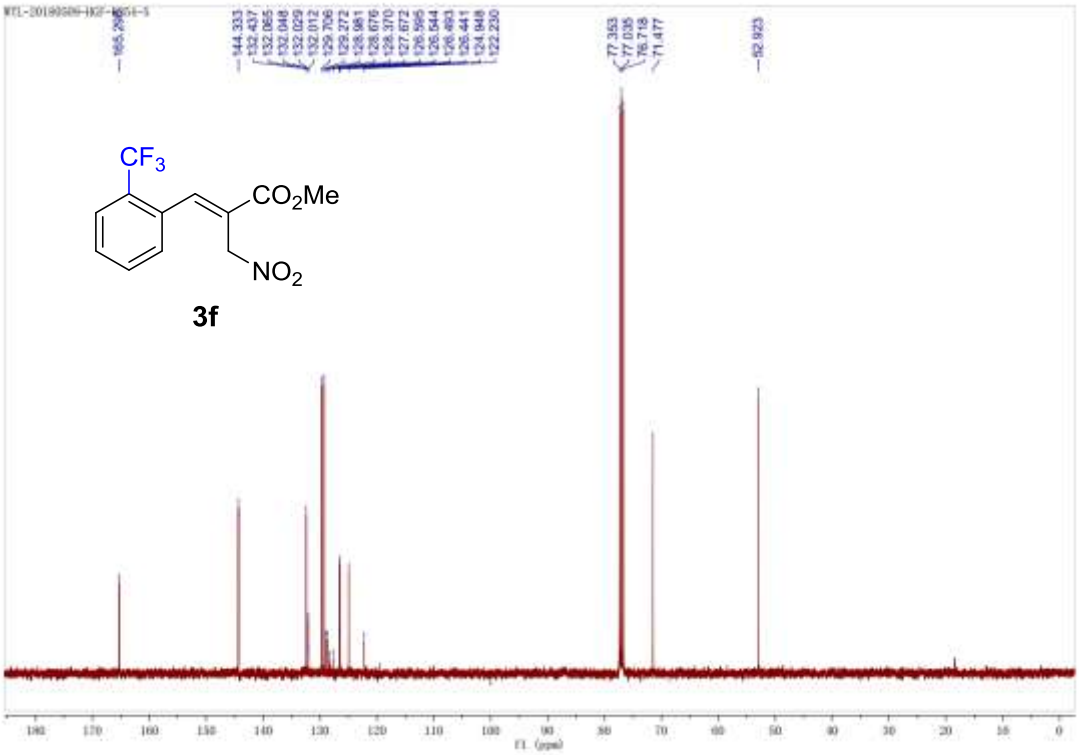

Cl
CO2Me
NO2
3d

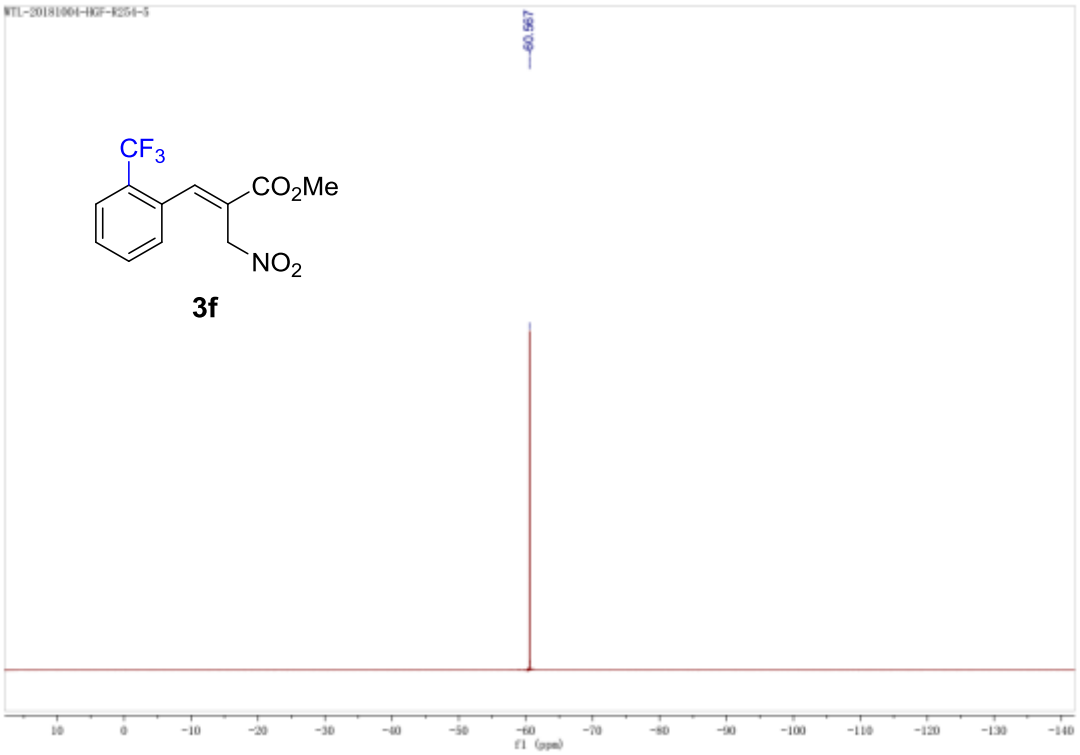

Cl
CO2Me
NO2
3d

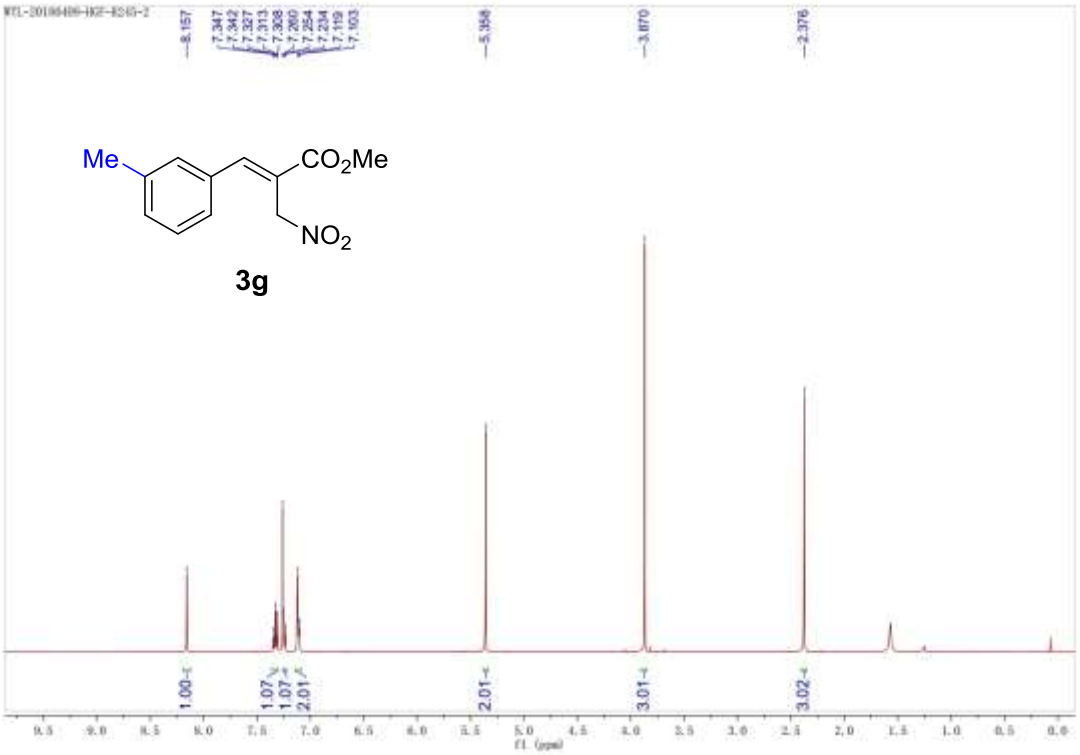

Br
CO2Me
NO2
3e


Br
CO2Me
NO2
3e

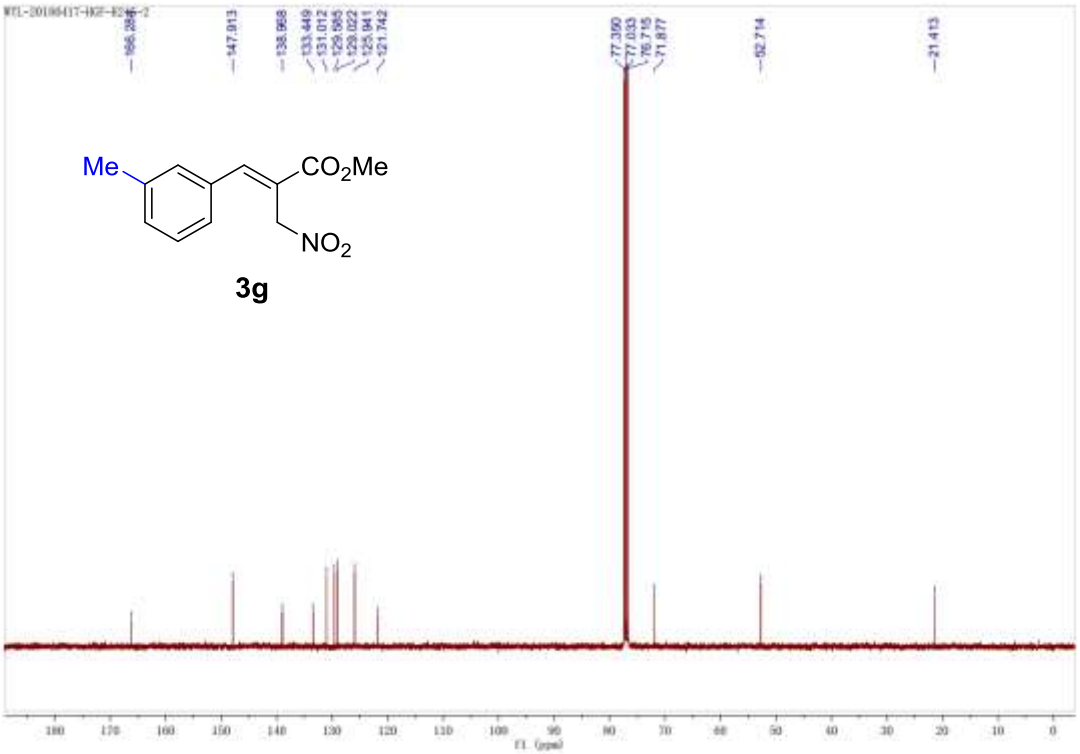

CF3
CO2Me
NO2
3f


CF3
CO2Me
NO2
3f

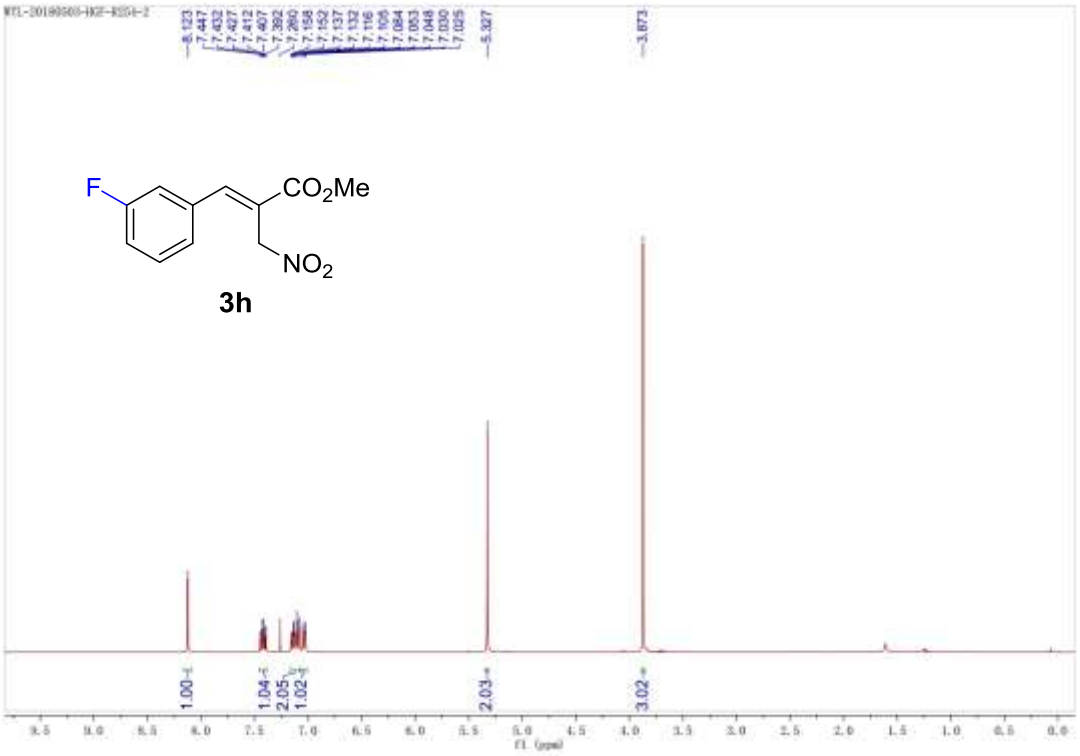

CF3
CO2Me
NO2
3f

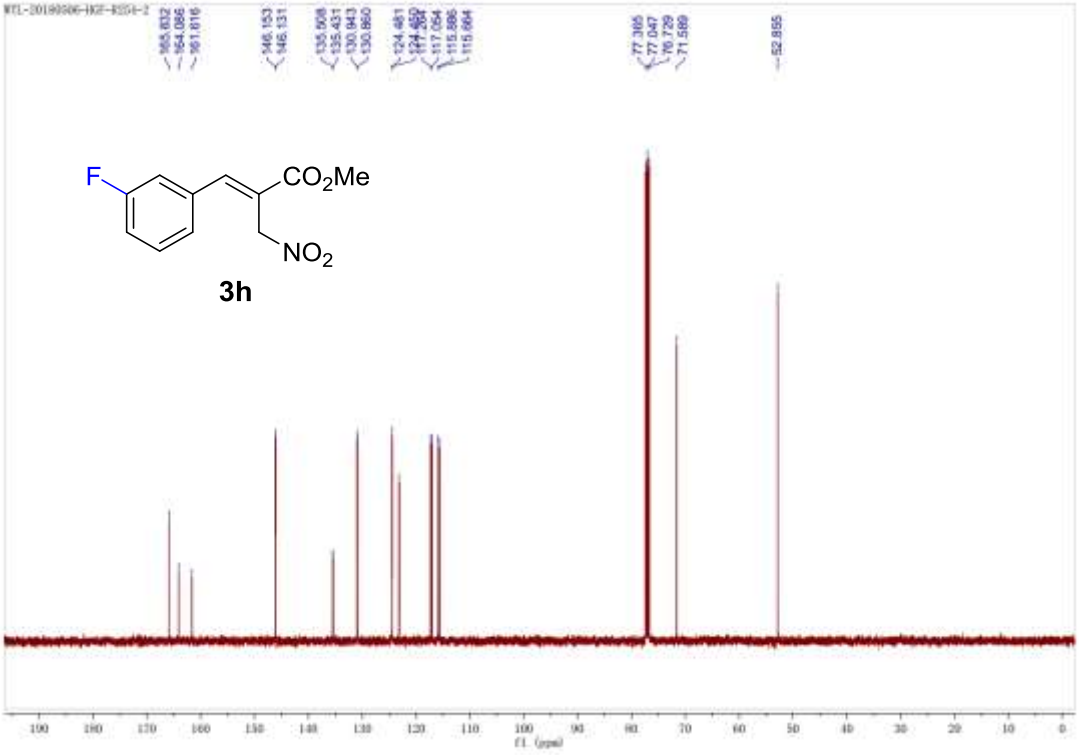

8.157
7.347
7.342
7.327
7.313
7.308
7.260
7.254
7.234
7.159
7.103
5.358
3.870
2.376
Me
CO2Me
NO2
1.00
1.07
1.07
2.01
2.01
3.01
3.02

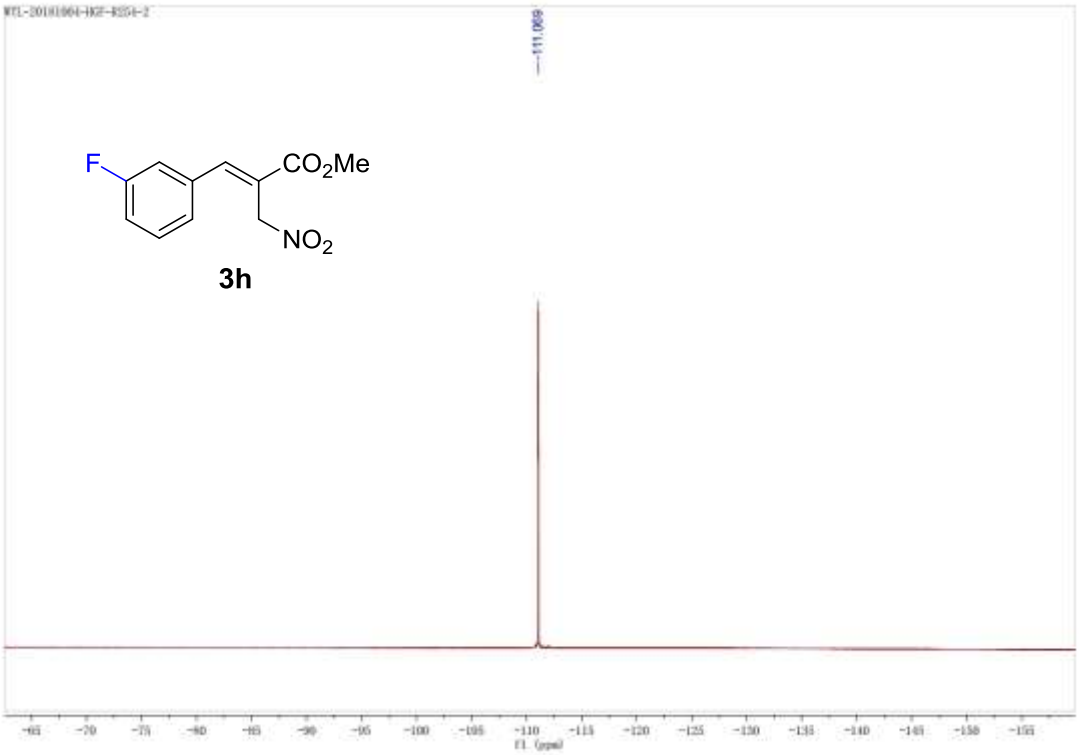
3g


147.913
138.968
133.449
131.012
129.585
129.022
125.941
121.742
77.390
77.033
76.715
71.877
62.714
21.413
Me
CO2Me
NO2

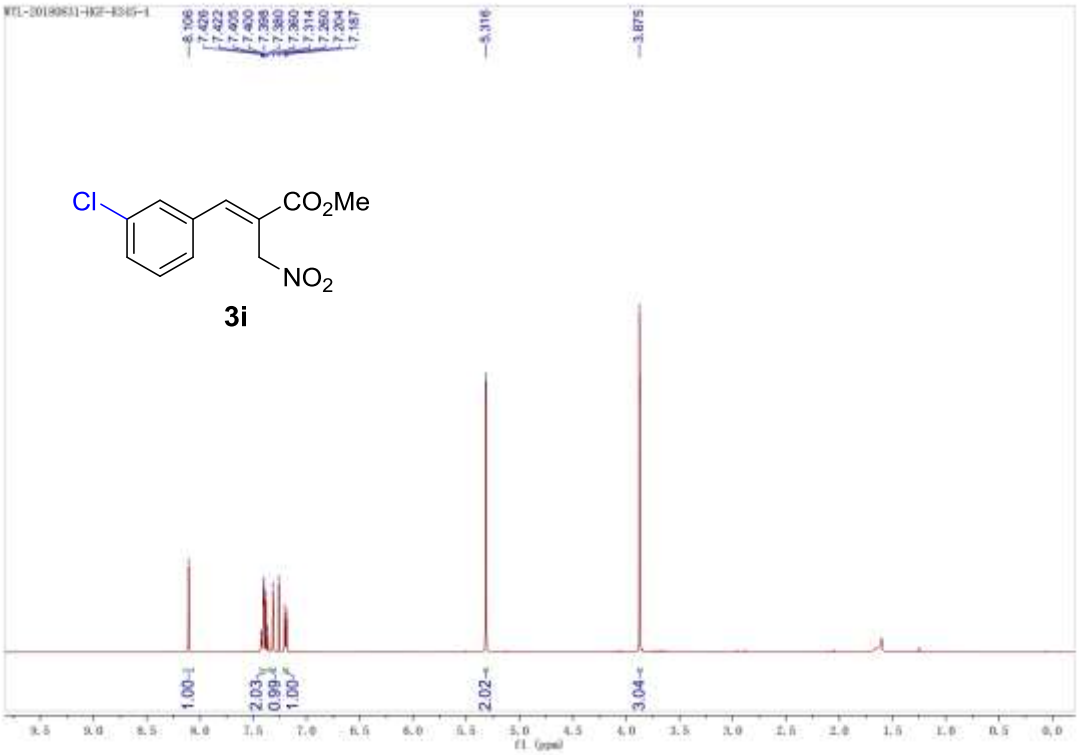
3g


F
CO2Me
NO2
3h

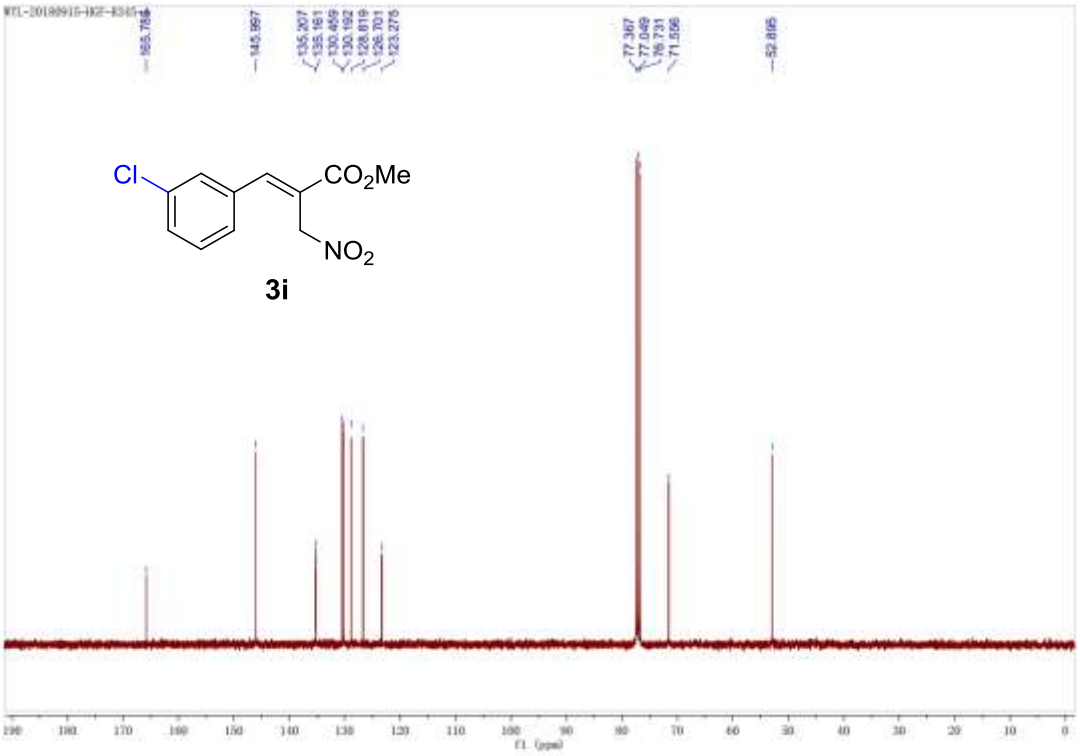

F
CO2Me
NO2
3h


F
CO2Me
NO2
-111.069

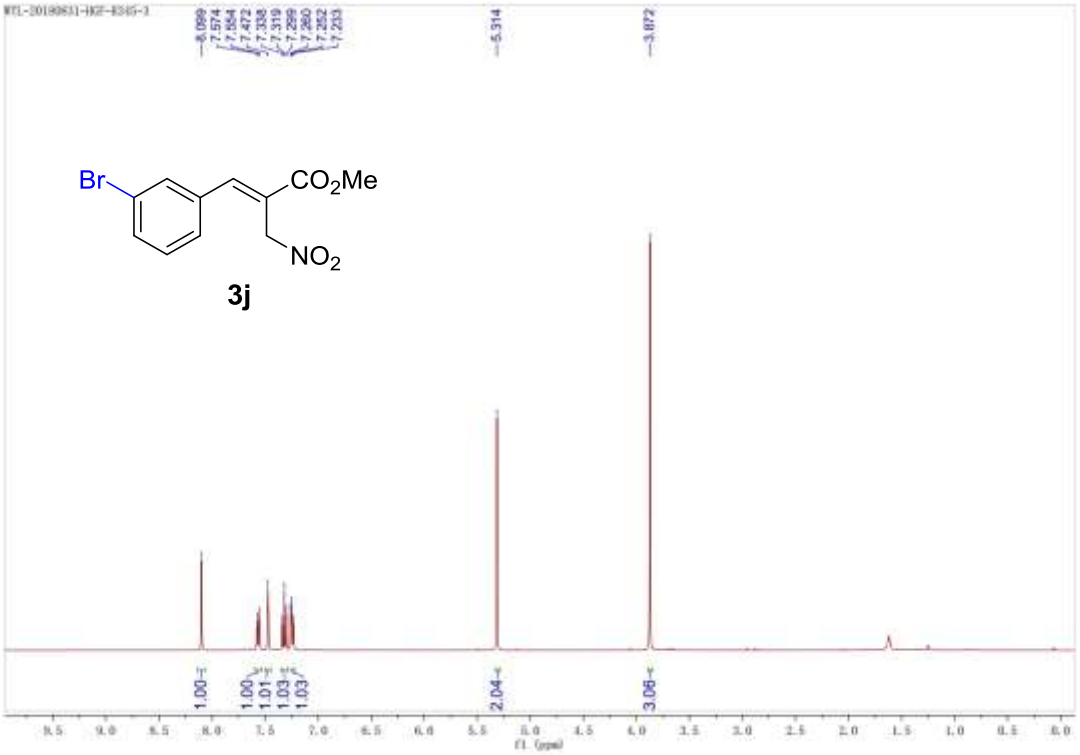
3h


Cl
CO2Me
NO2
8.106
7.426
7.422
7.405
7.400
7.388
7.380
7.360
7.314
7.260
7.204
7.187
5.316
3.875
1.00
2.03
0.99
1.00
2.02
3.04

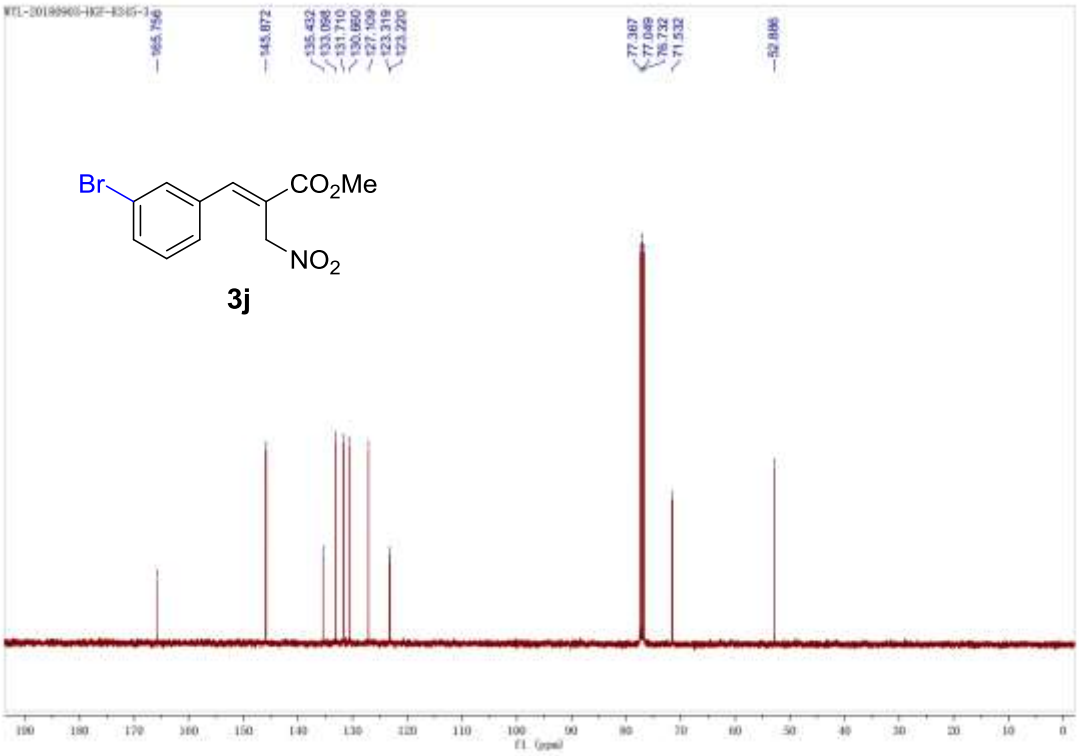
3i



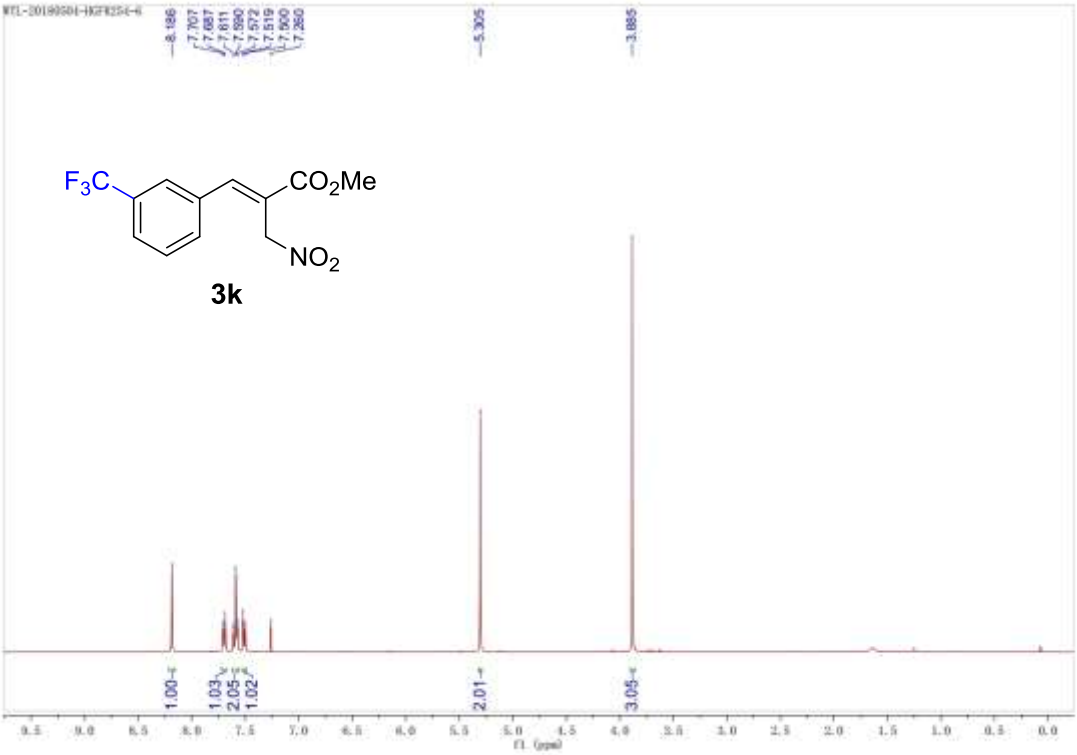
3i



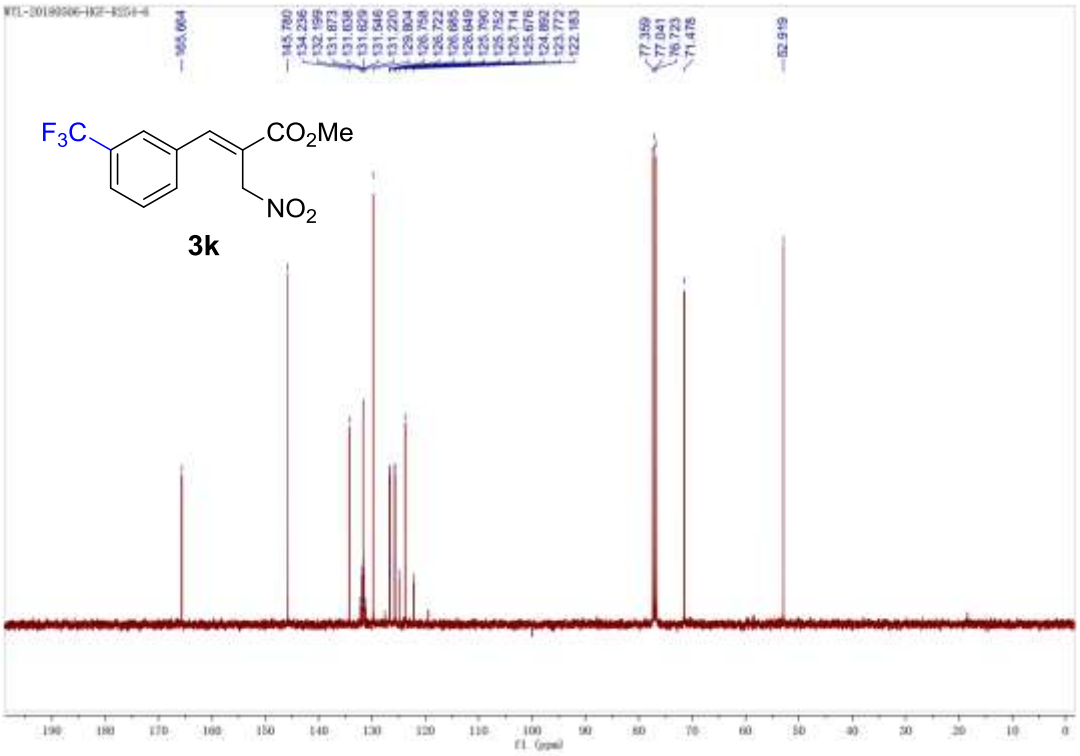
3j

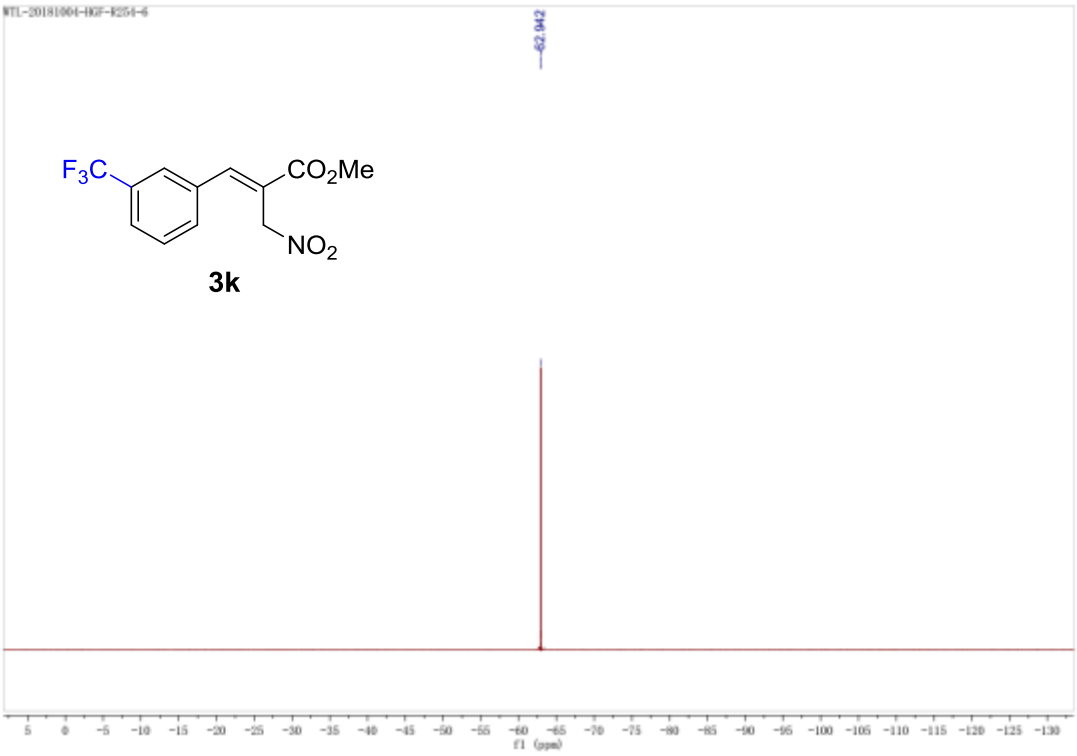


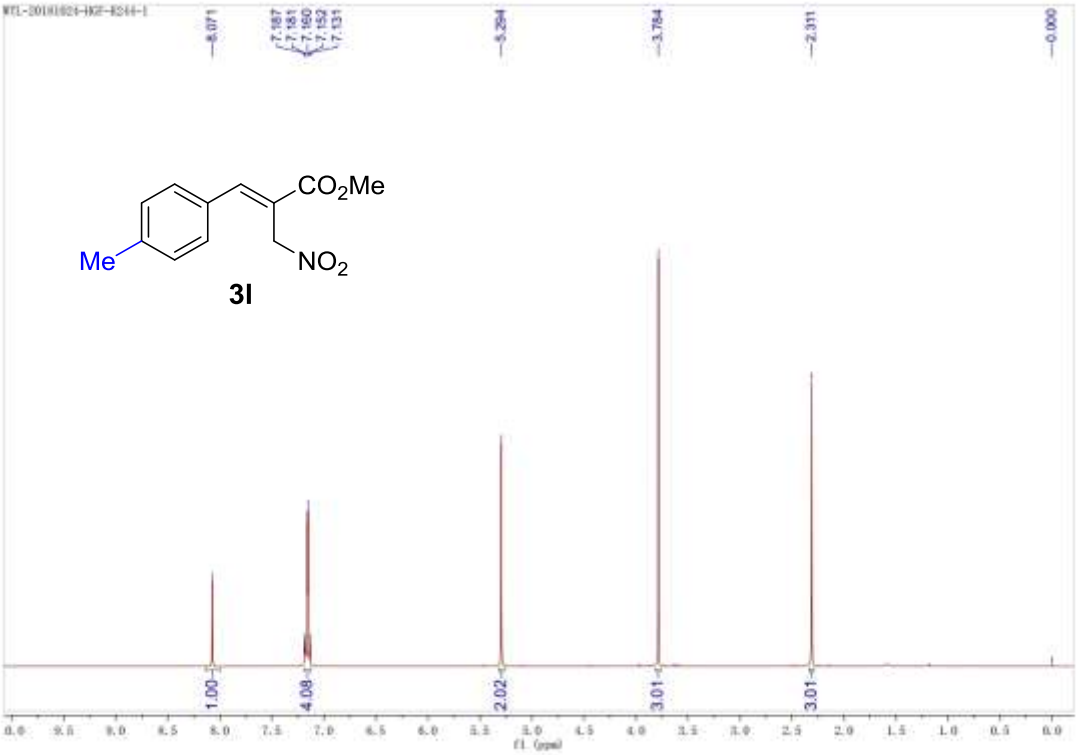
3j

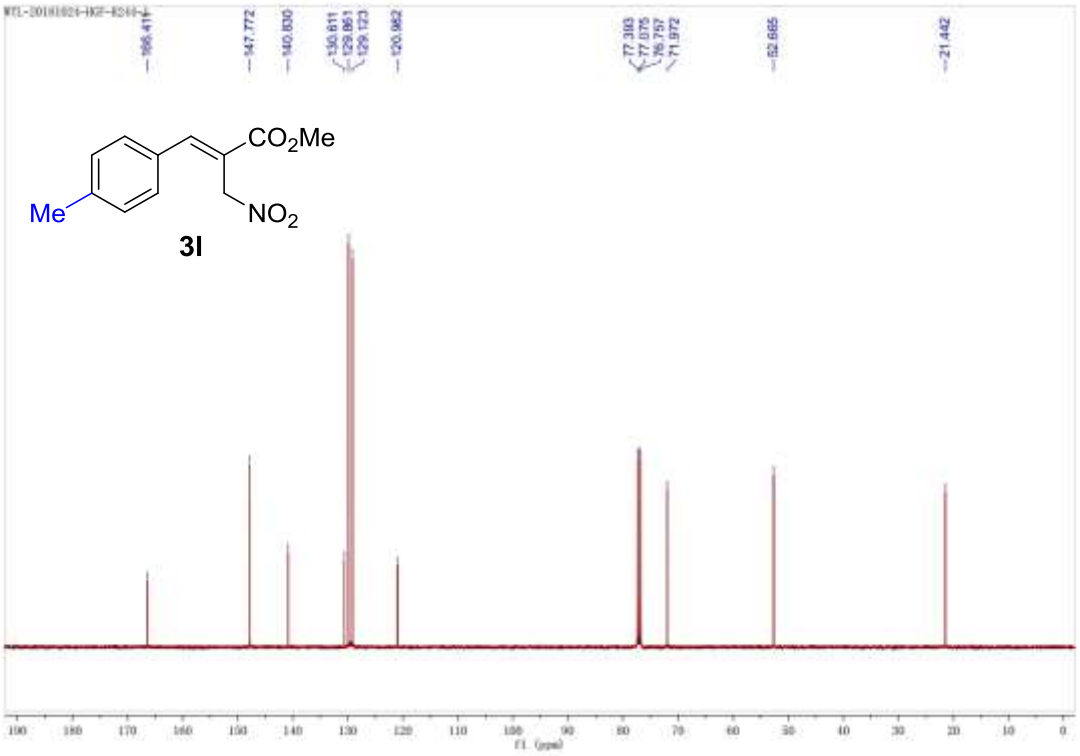


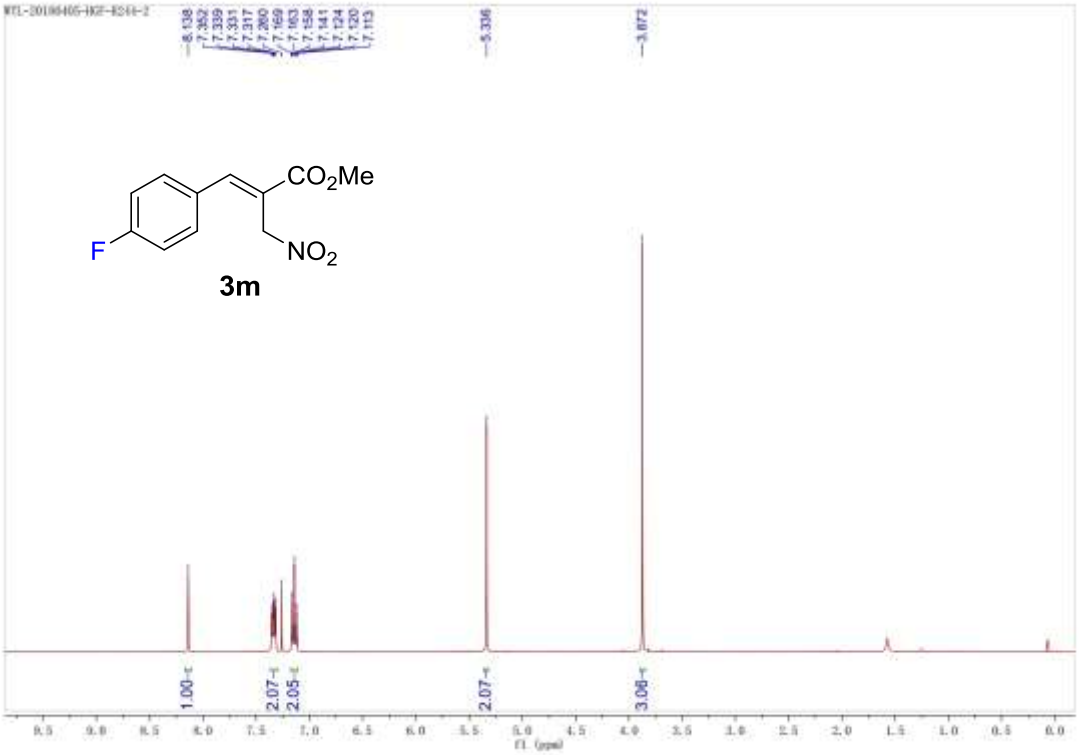
3k

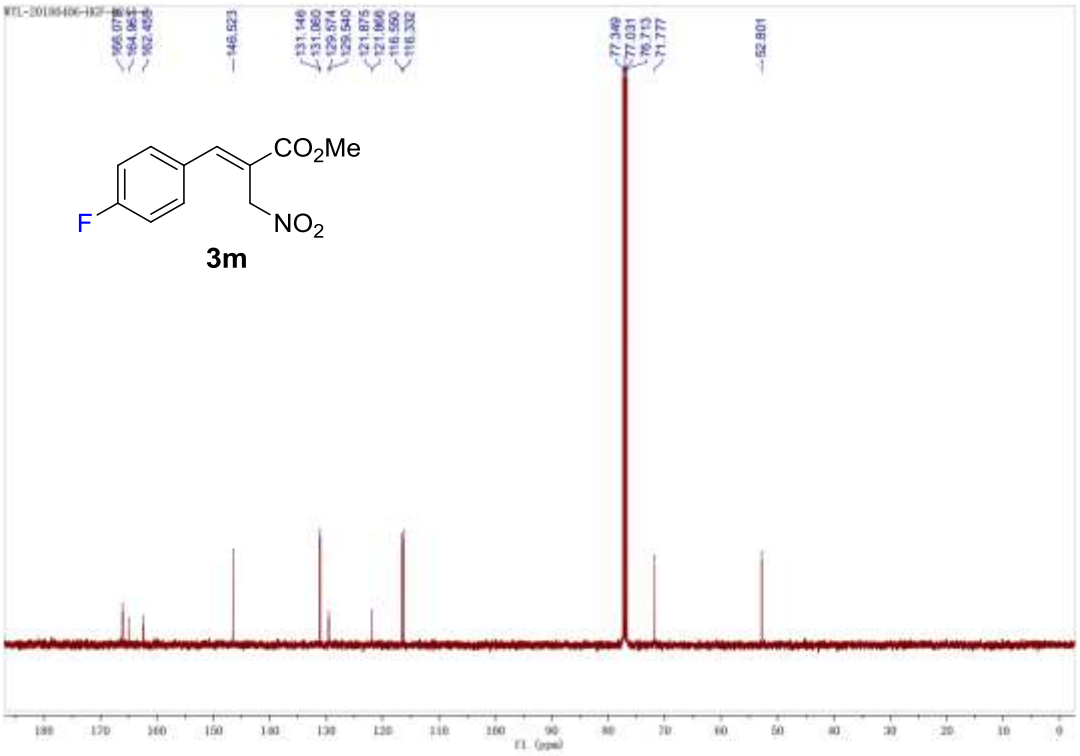

F3C
CO2Me
NO2
3k

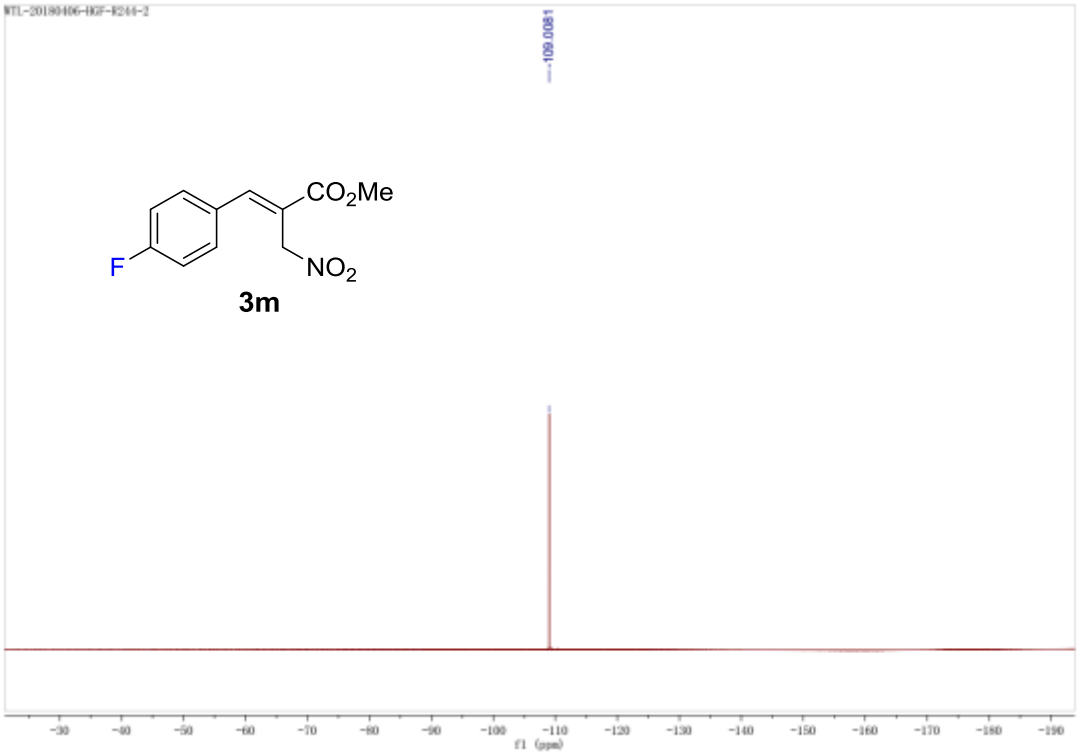

-62.942
F3C
CO2Me
NO2
3k

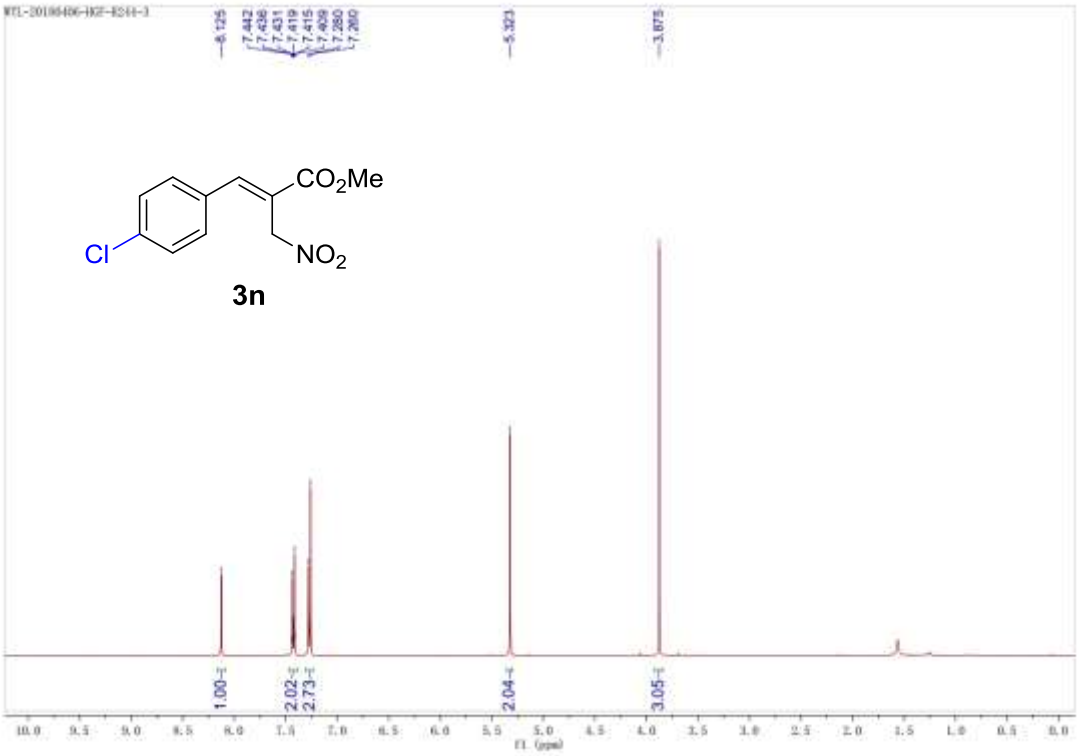

8.071
7.187
7.161
7.160
7.152
7.131
5.294
3.784
2.311
0.000
CO2Me
Me
NO2
3l
1.00
4.08
2.02
3.01
3.01

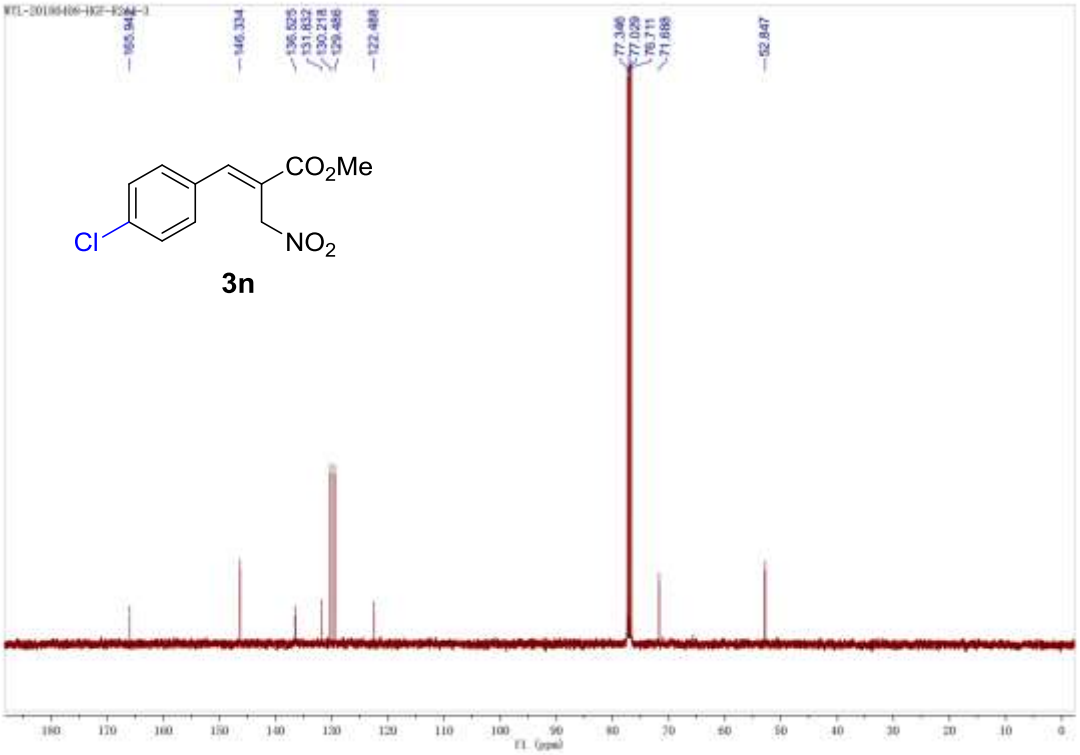

166.417
147.772
140.030
130.611
129.861
129.123
120.982
77.393
77.075
76.757
71.972
52.665
21.442
CO2Me
Me
NO2
3l

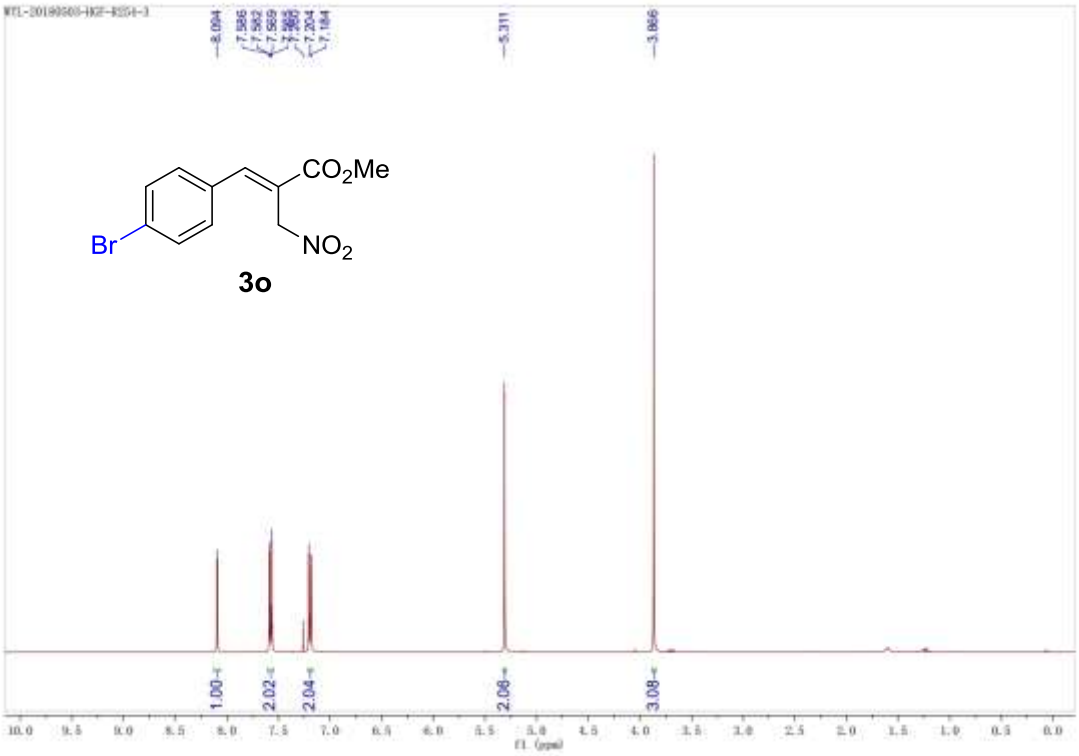

8.138
7.352
7.339
7.331
7.317
7.260
7.169
7.163
7.158
7.141
7.124
7.120
7.113
5.336
3.672
CO2Me
F
NO2
3m
1.00
2.07
2.05
2.07
3.06

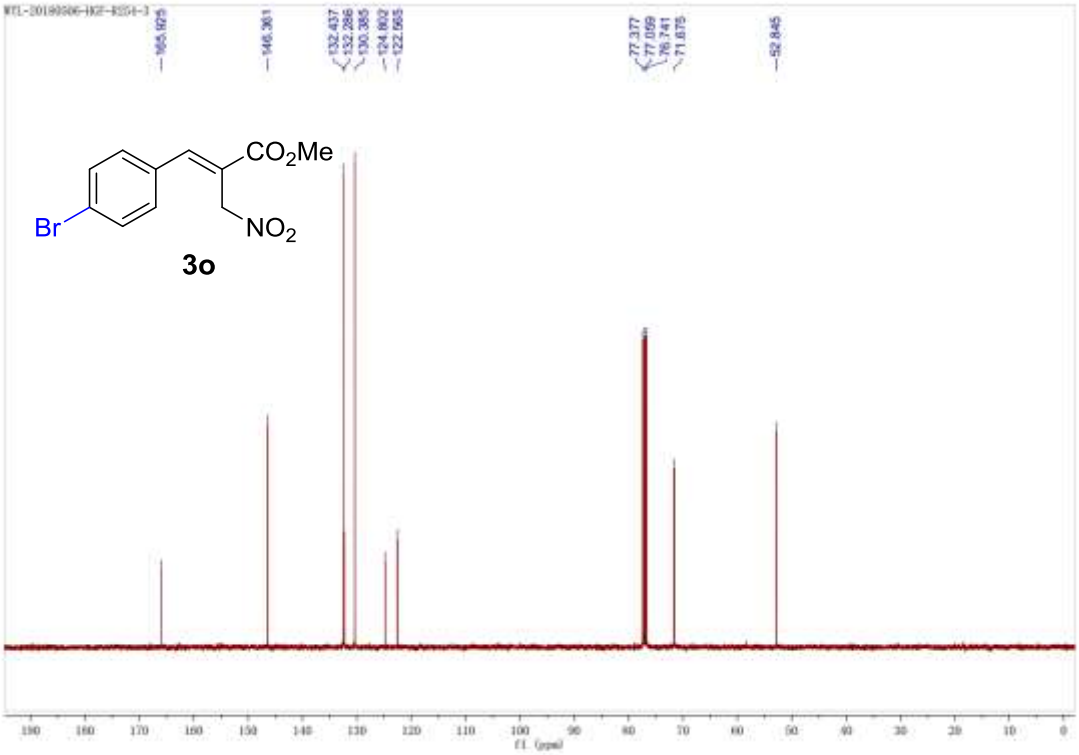

CO2Me
F
NO2
3m

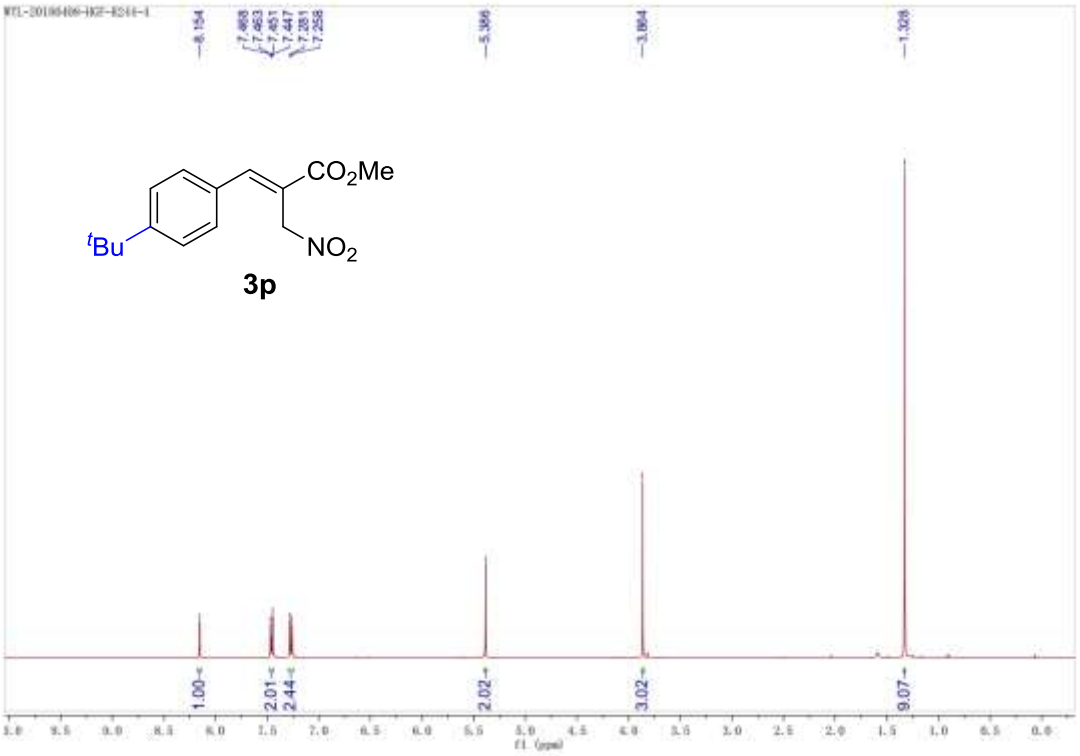

CO2Me
F
NO2
3m

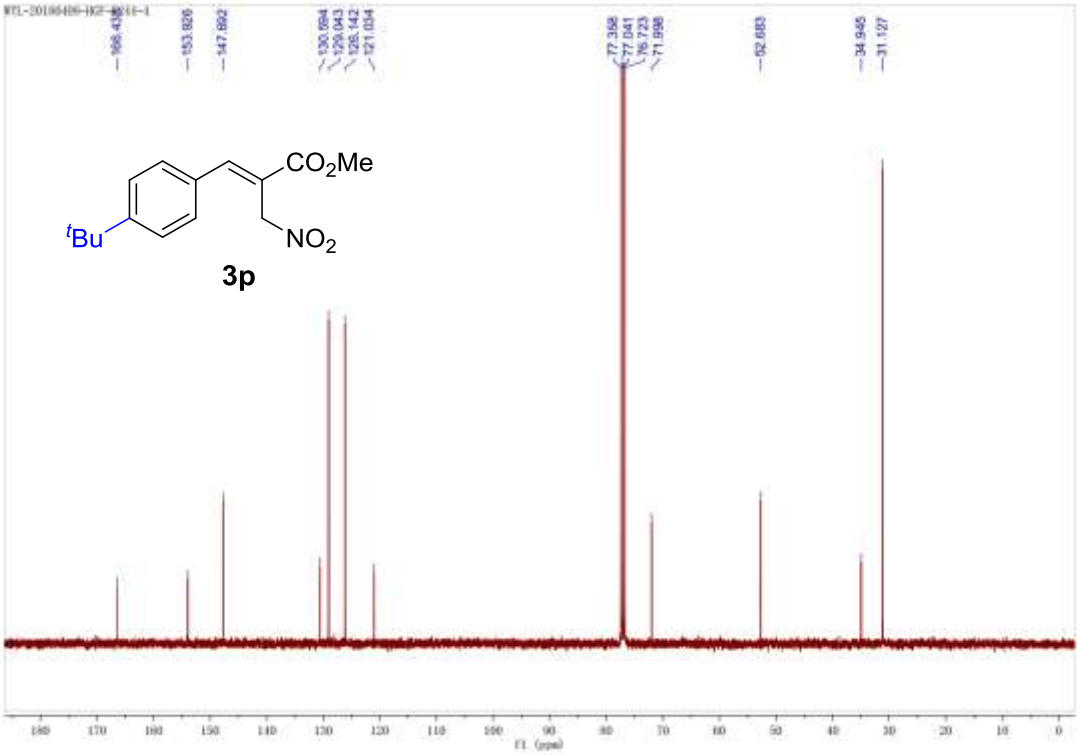

8.125
7.442
7.436
7.431
7.419
7.415
7.409
7.280
7.260
5.323
3.875
CO2Me
Cl
NO2
3n
1.00
2.02
2.73
2.04
3.05

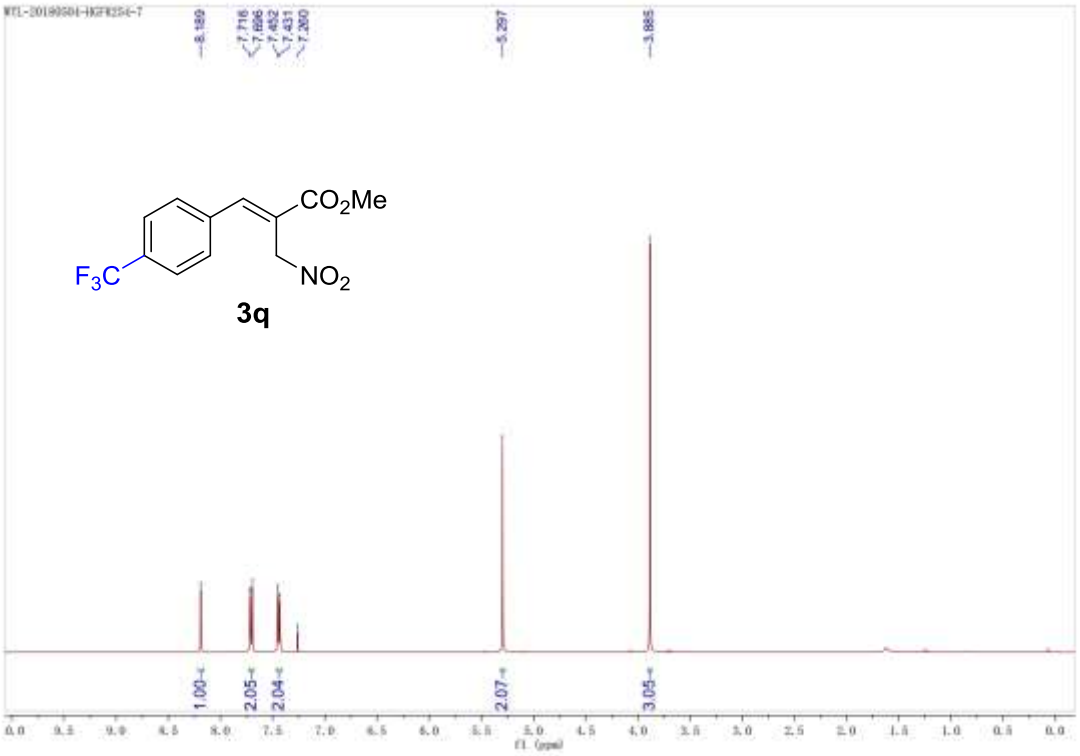

165.942
146.334
136.525
131.632
130.218
129.486
122.488
77.346
77.029
76.711
71.688
52.847
CO2Me
Cl
NO2
3n

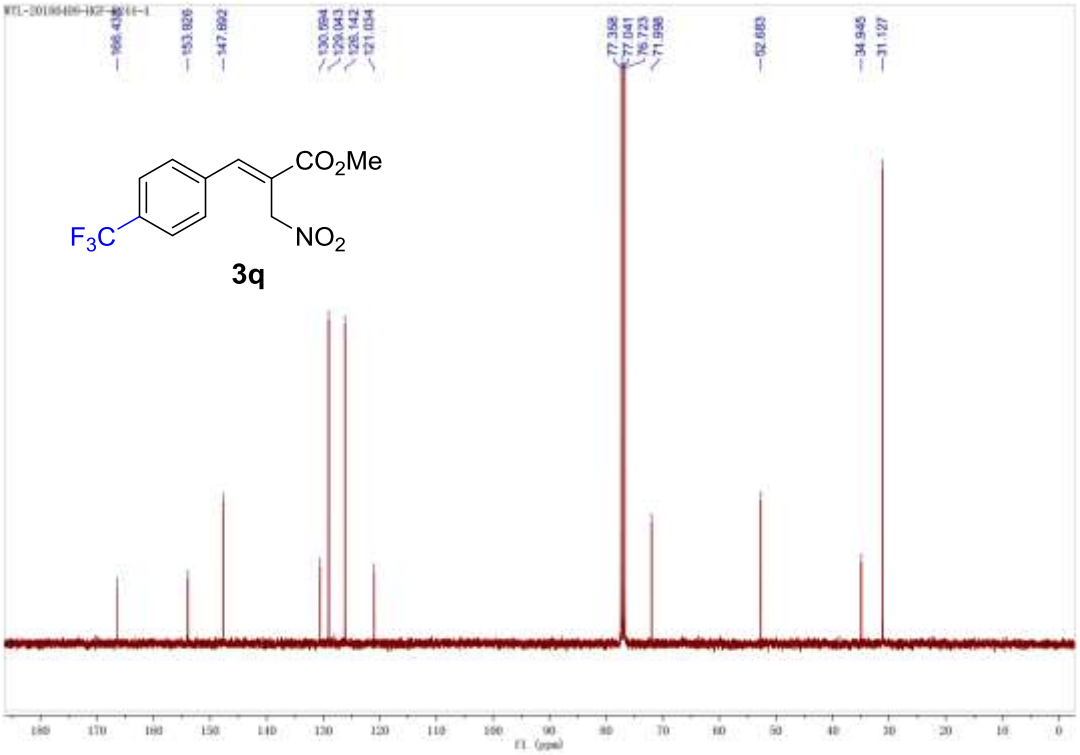

8.094
7.586
7.582
7.569
7.204
7.184
5.311
3.866
CO2Me
Br
NO2
3o
1.00
2.02
2.04
2.06
3.08

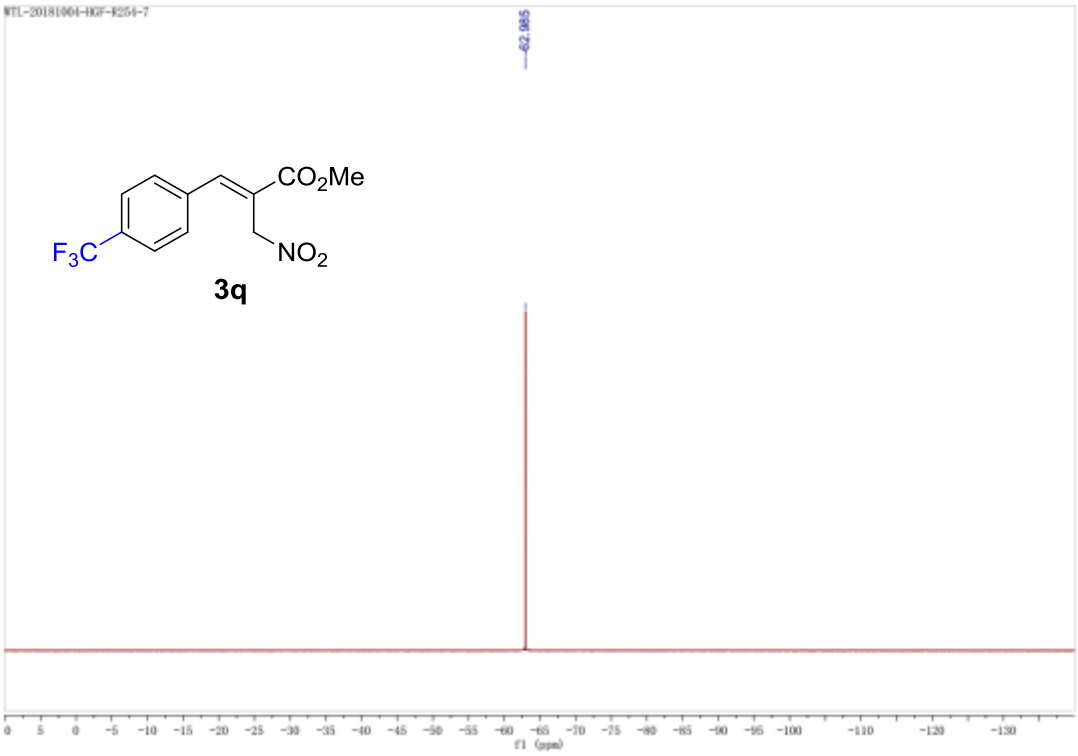

165.925
146.361
132.437
132.286
130.365
124.802
122.565
77.377
77.059
76.741
71.675
52.845
CO2Me
Br
NO2
3o

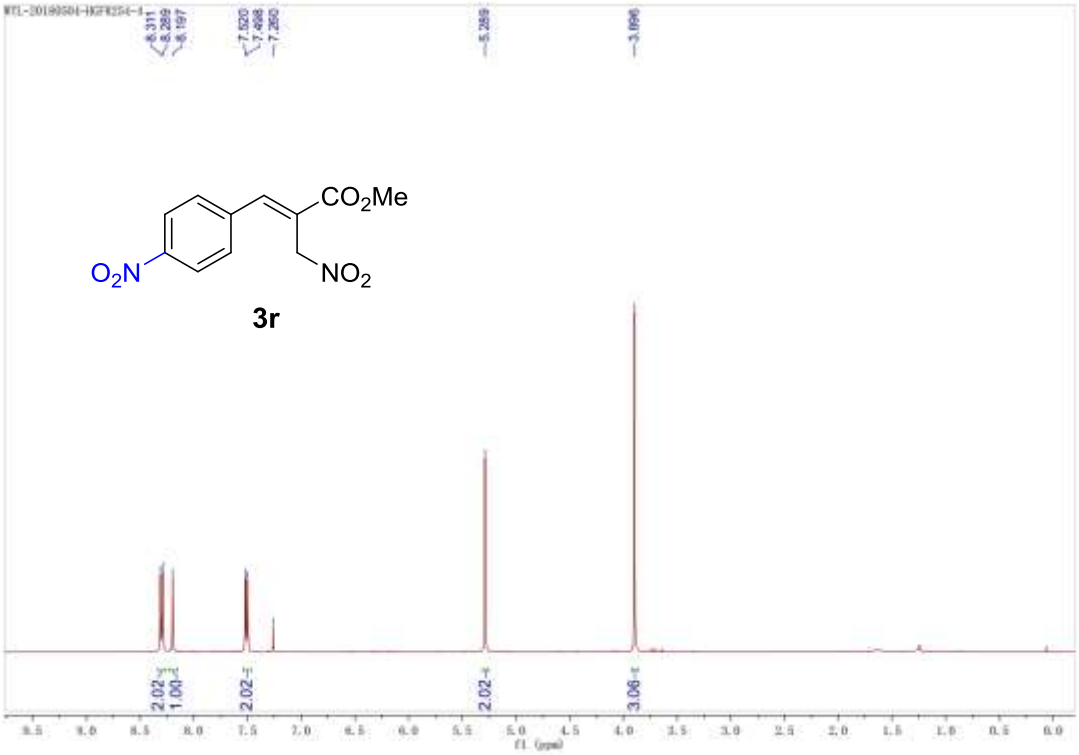

8.154
7.466
7.463
7.451
7.447
7.281
7.258
5.366
3.864
1.308
CO2Me
tBu
NO2
3p
1.00
2.01
2.44
2.02
3.02
9.07
f1 (ppm)

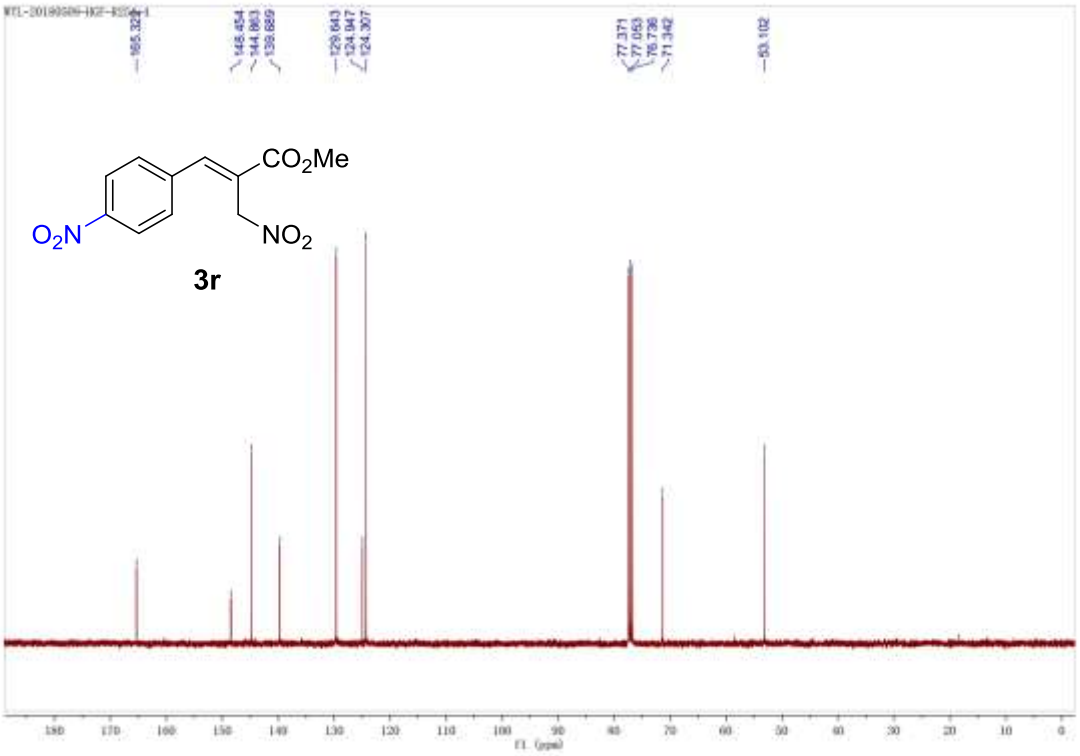

166.438
153.826
147.892
130.684
129.043
128.142
121.034
77.358
77.041
76.723
71.998
62.883
34.945
31.127
CO2Me
tBu
NO2
3p
f1 (ppm)

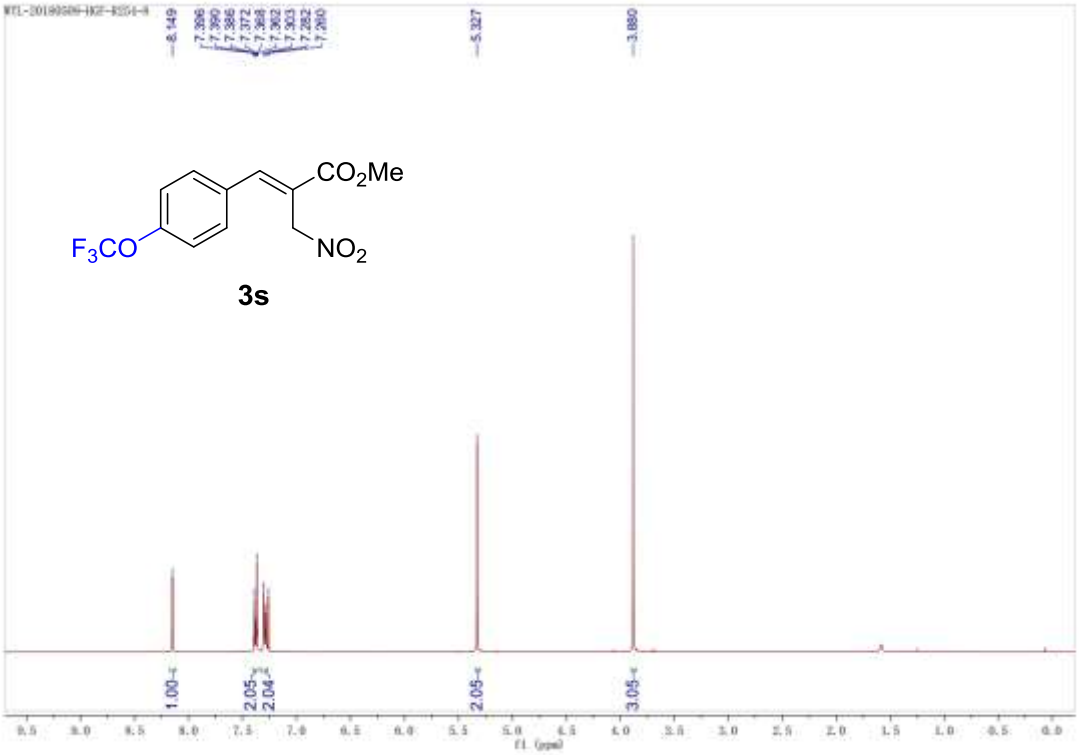

8.189
7.716
7.696
7.452
7.431
7.260
5.297
3.885
CO2Me
F3C
NO2
3q
1.00
2.05
2.04
2.07
3.05

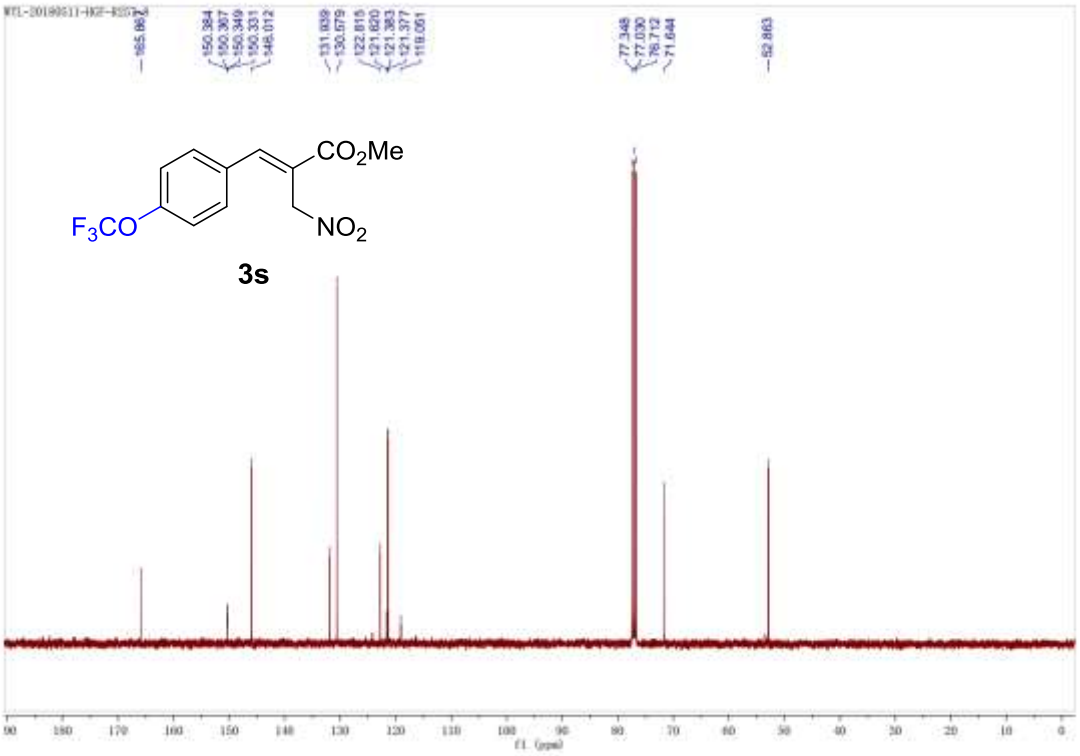

166.438
153.826
147.892
130.684
129.043
126.142
121.034
77.358
77.041
76.723
71.998
52.883
34.945
31.127
CO2Me
F3C
NO2
3q

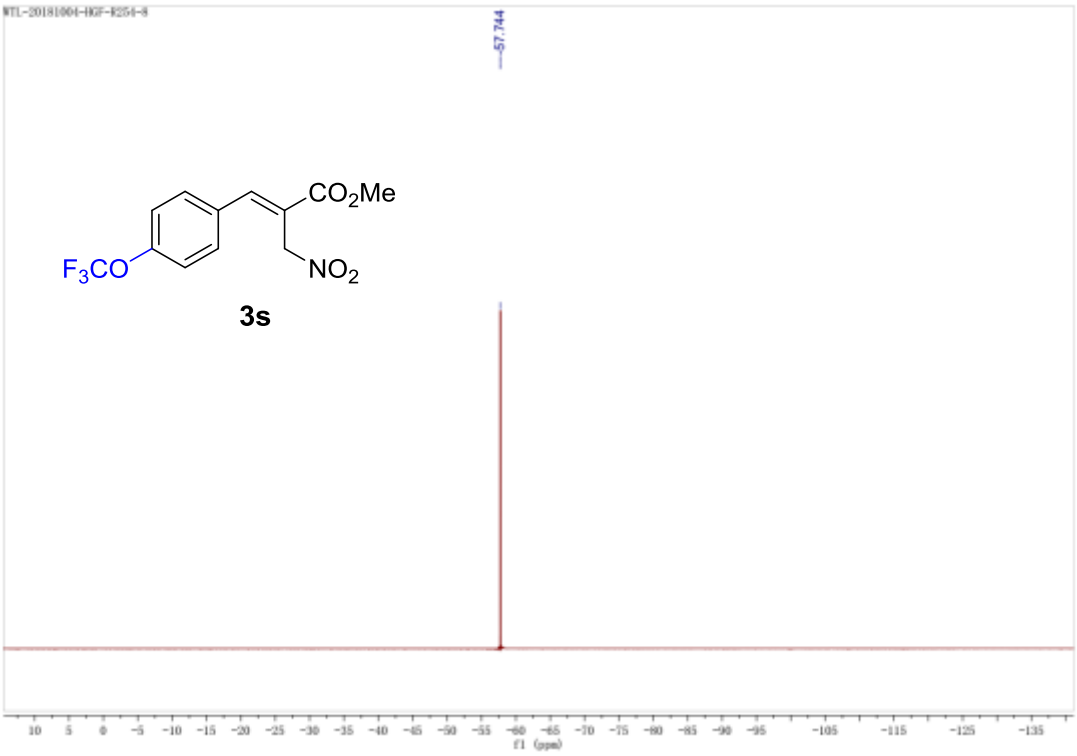

CO2Me
F3C
NO2
3q

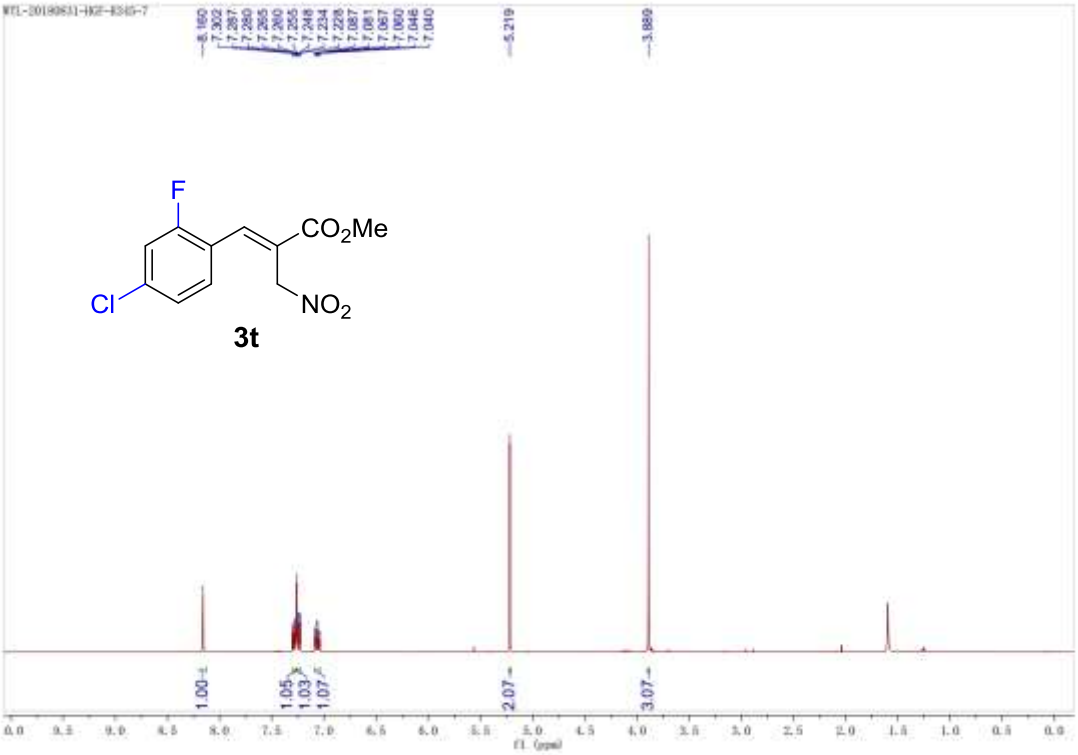

CO2Me
O2N
NO2
3r

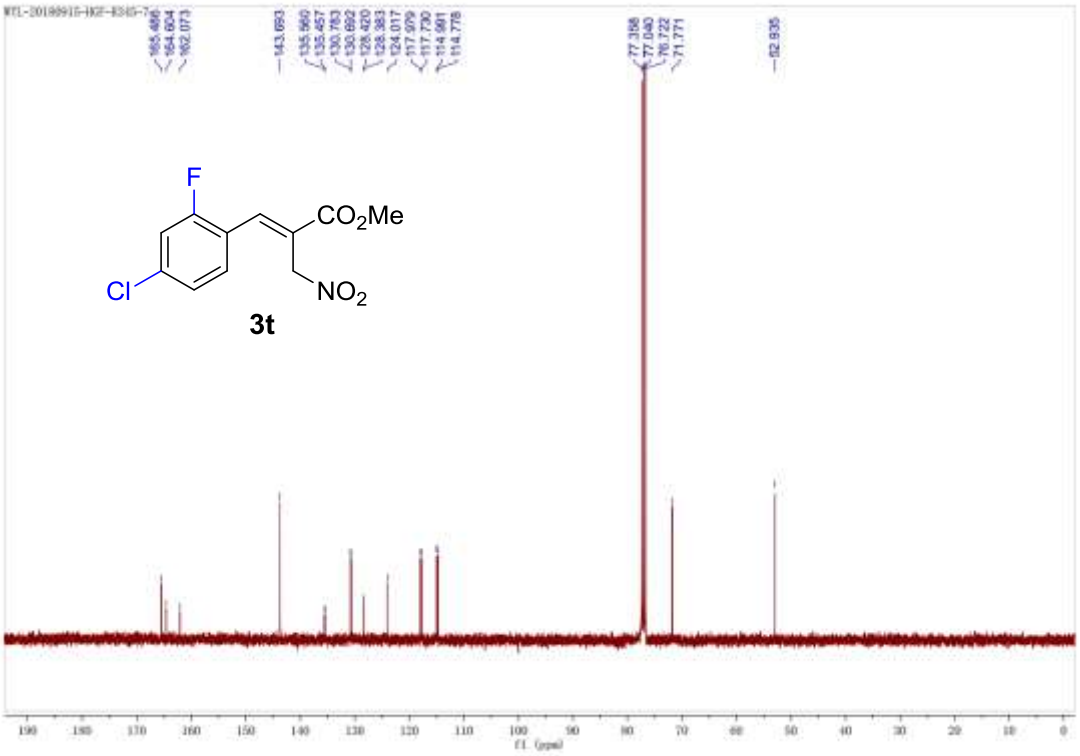

165.324
148.454
144.863
139.689
129.643
124.947
124.307
77.371
77.053
76.736
71.342
53.102
CO2Me
O2N
NO2
3r

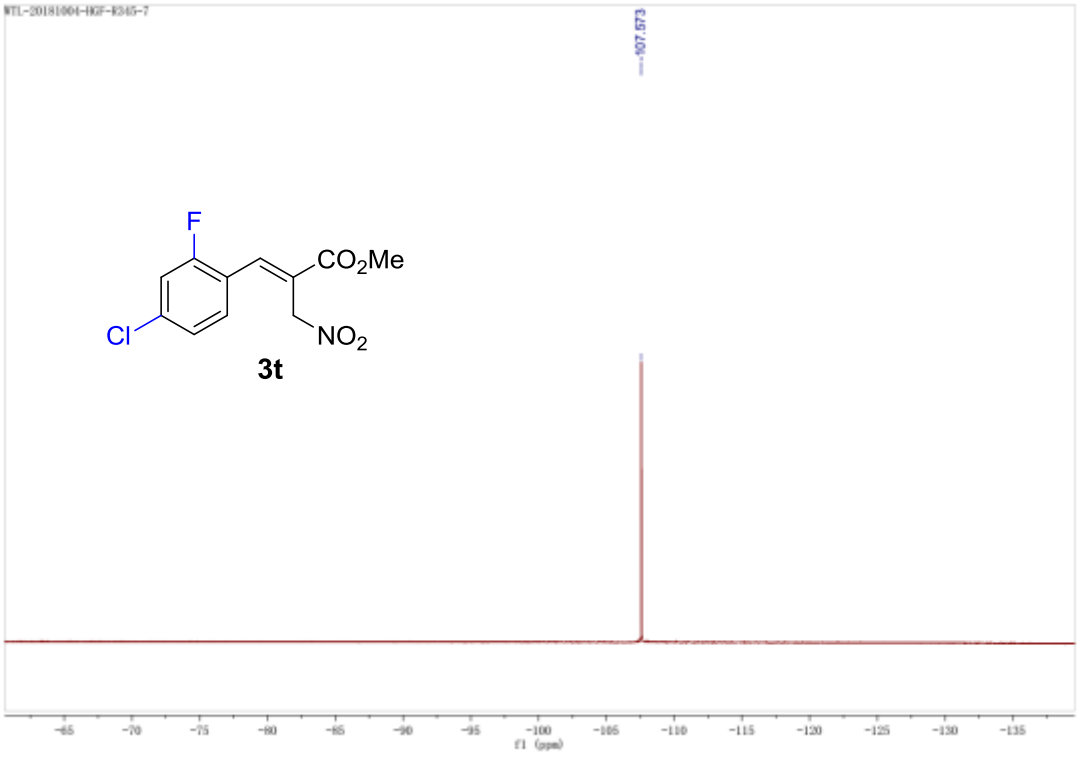

8.149
7.396
7.390
7.386
7.372
7.368
7.362
7.303
7.282
7.260
5.327
3.880
CO2Me
F3CO
NO2
3s
1.00
2.05
2.04
2.05
3.05

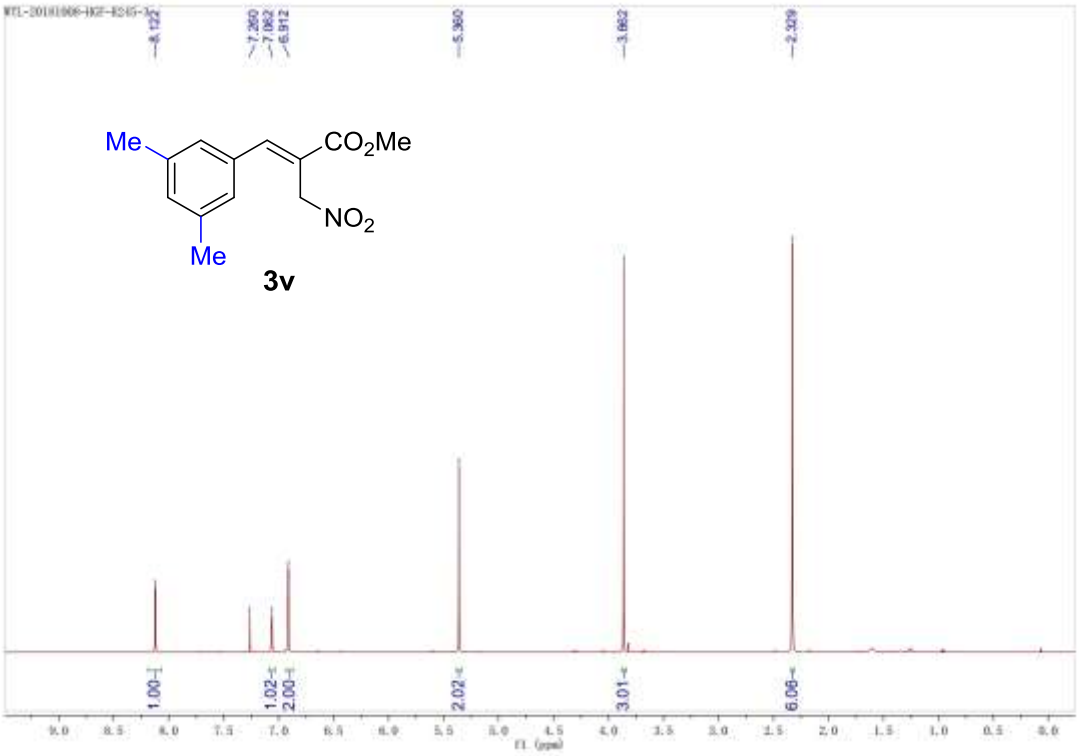

165.862
150.384
150.367
150.349
150.331
148.012
131.839
130.679
122.615
121.620
121.383
121.377
119.061
77.348
77.030
76.712
71.644
62.863
CO_2Me
F_3CO
NO_2
3s

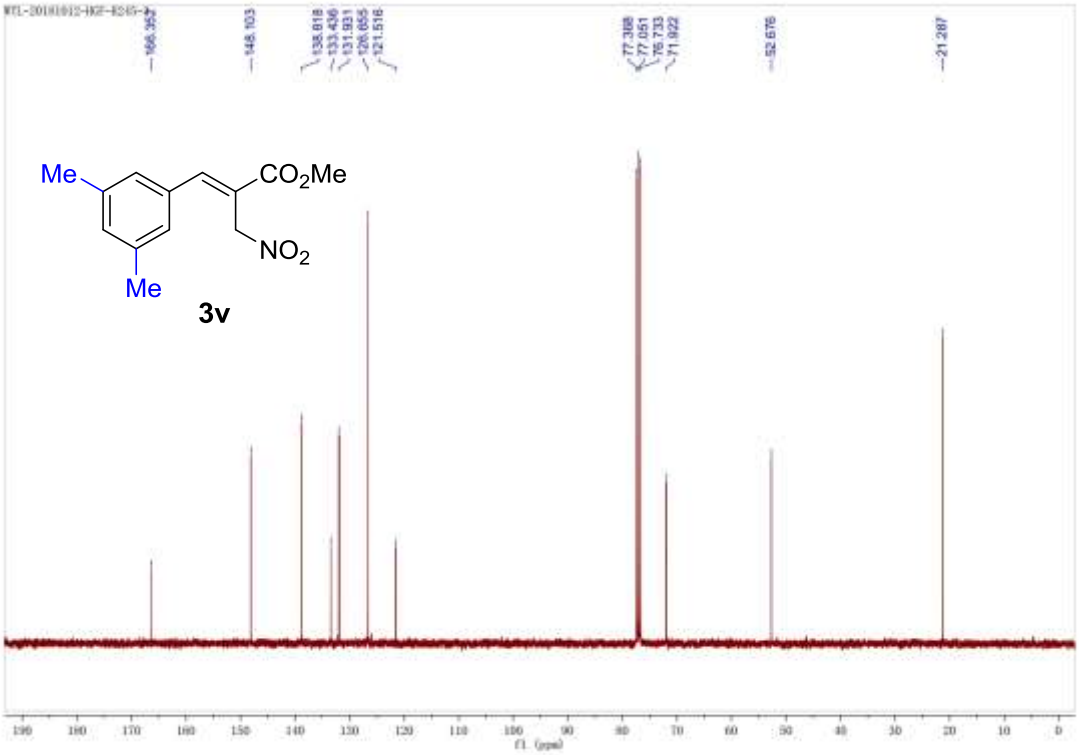

-57.744
CO2Me
F3CO
NO2
3s

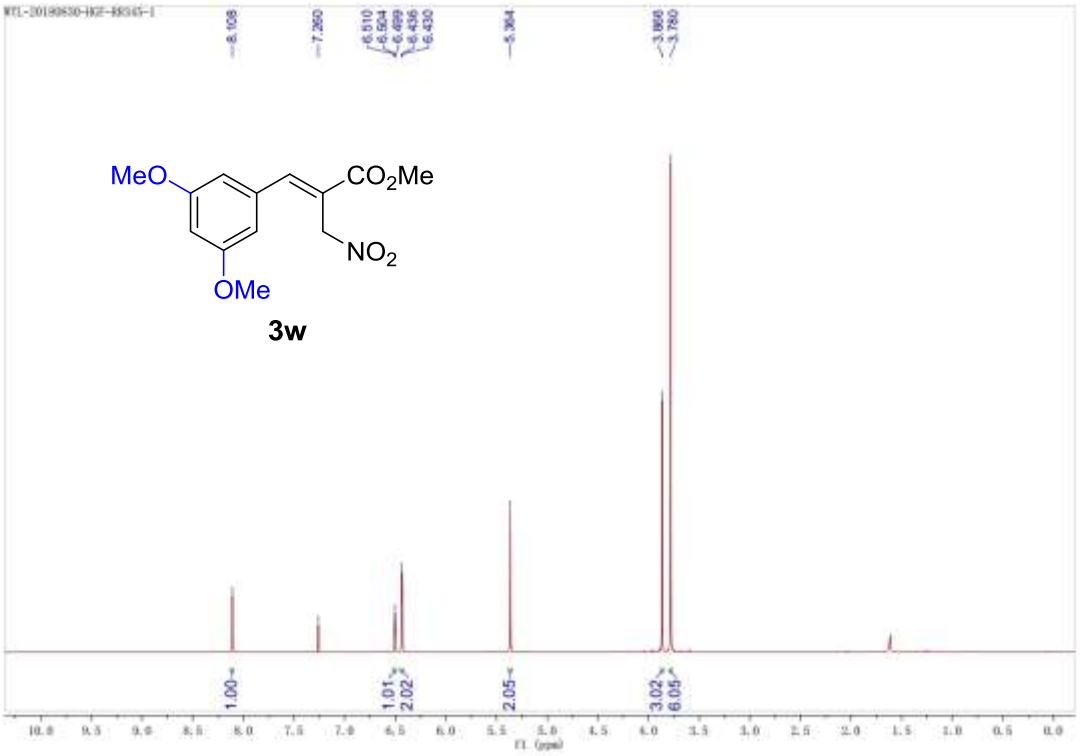

8.160
7.302
7.287
7.280
7.265
7.260
7.255
7.248
7.234
7.228
7.087
7.081
7.067
7.060
7.046
7.040
5.219
3.880
F
CO2Me
Cl
NO2
3t
1.00
1.05
1.03
1.07
2.07
3.07

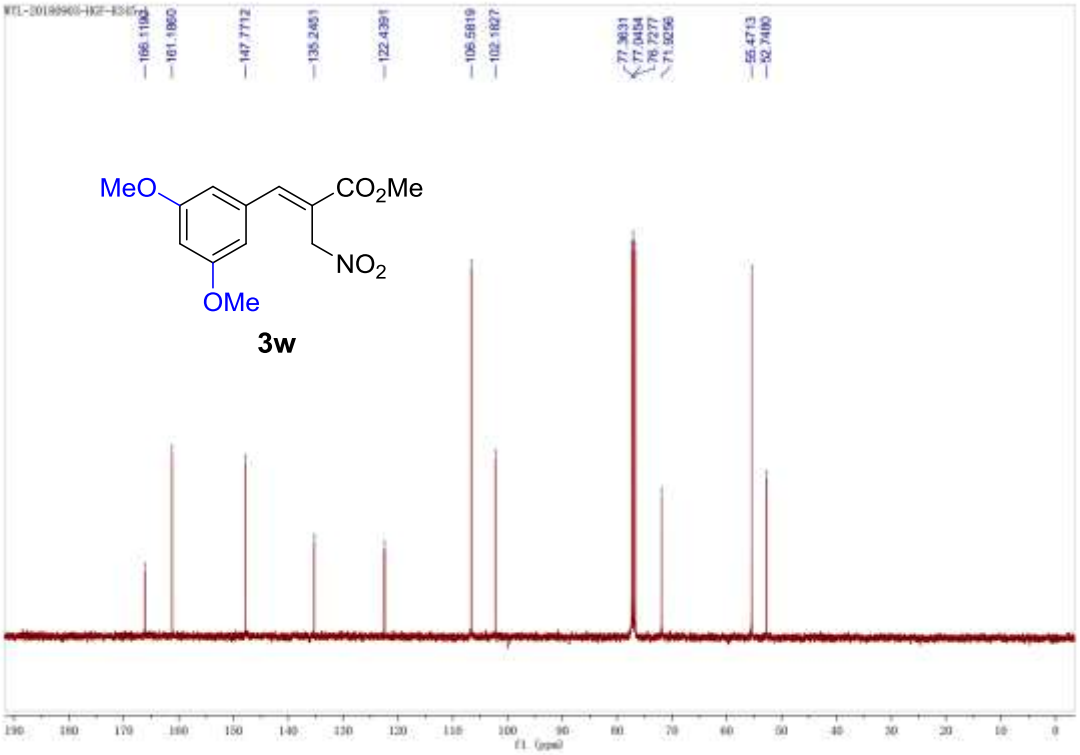

F
CO2Me
Cl
NO2
3t

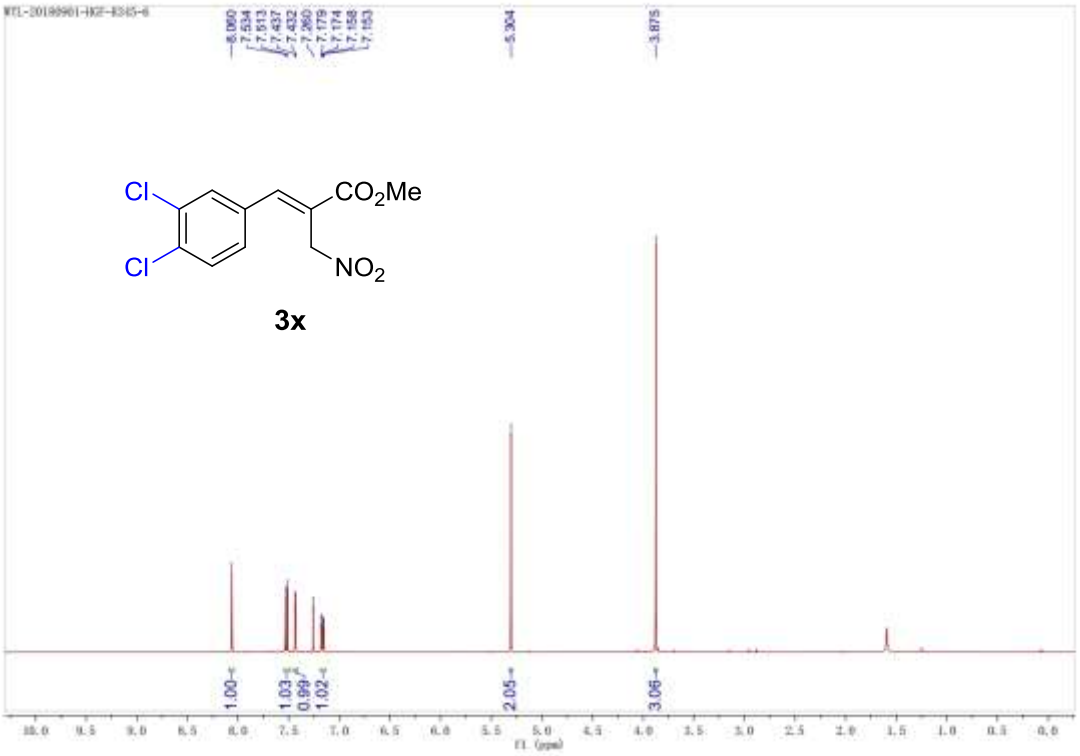

F
CO2Me
Cl
NO2
3t

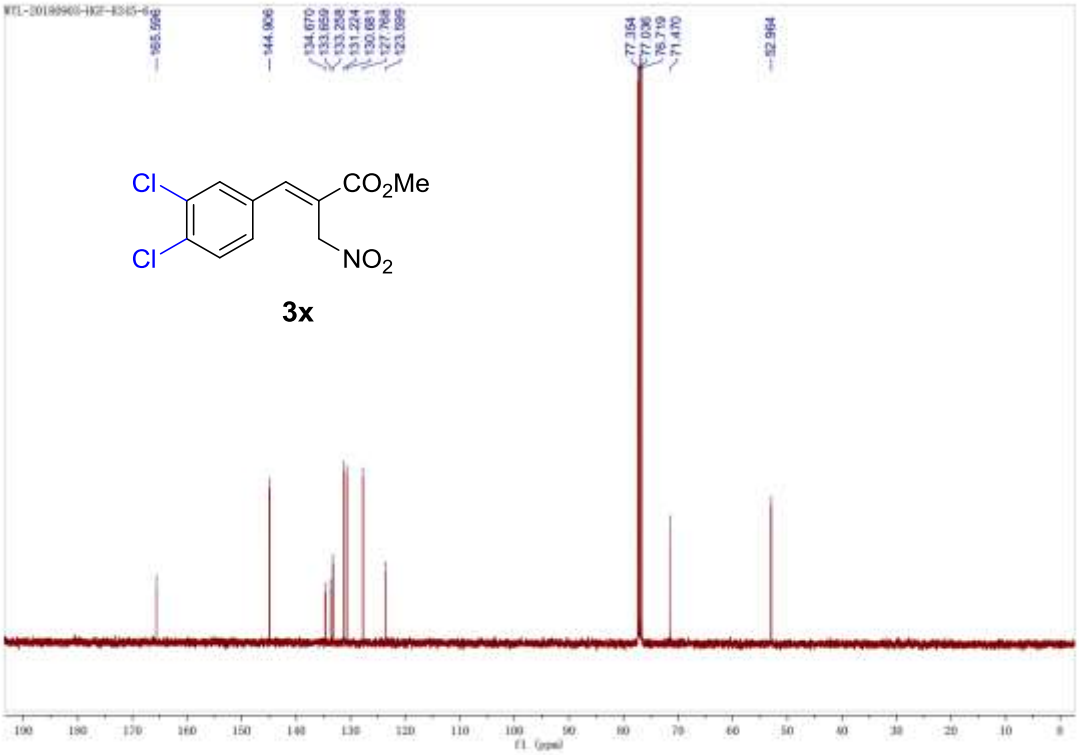

Me
CO2Me
NO2
Me
3v

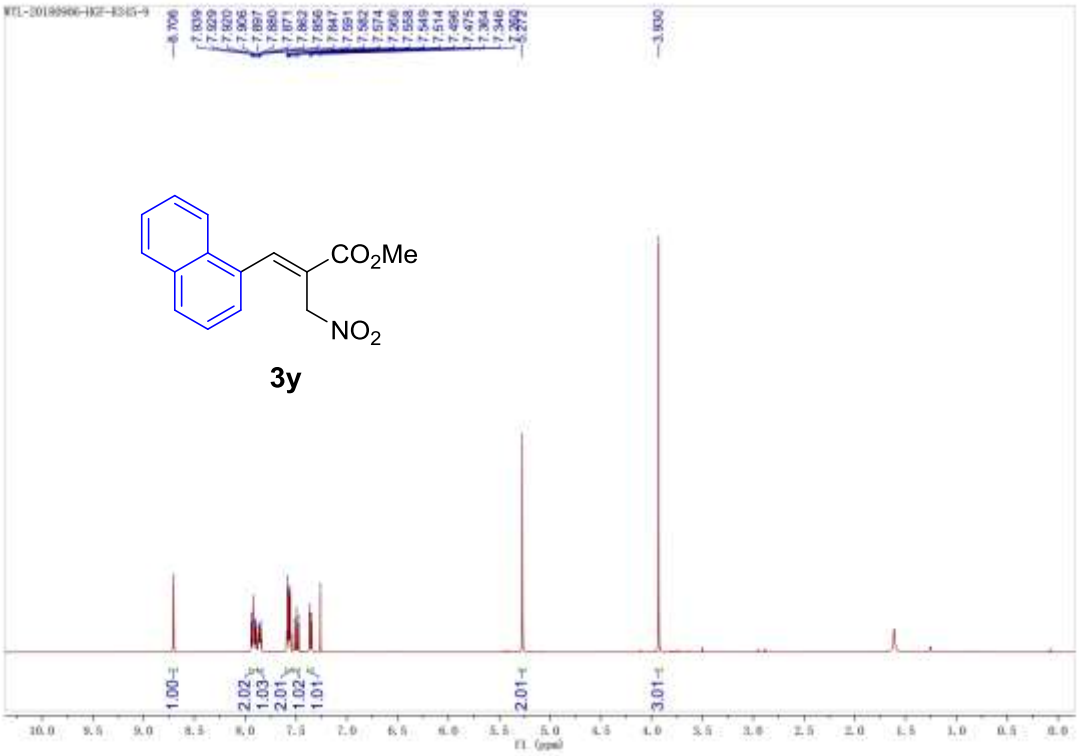

Me
CO2Me
NO2
Me
3v

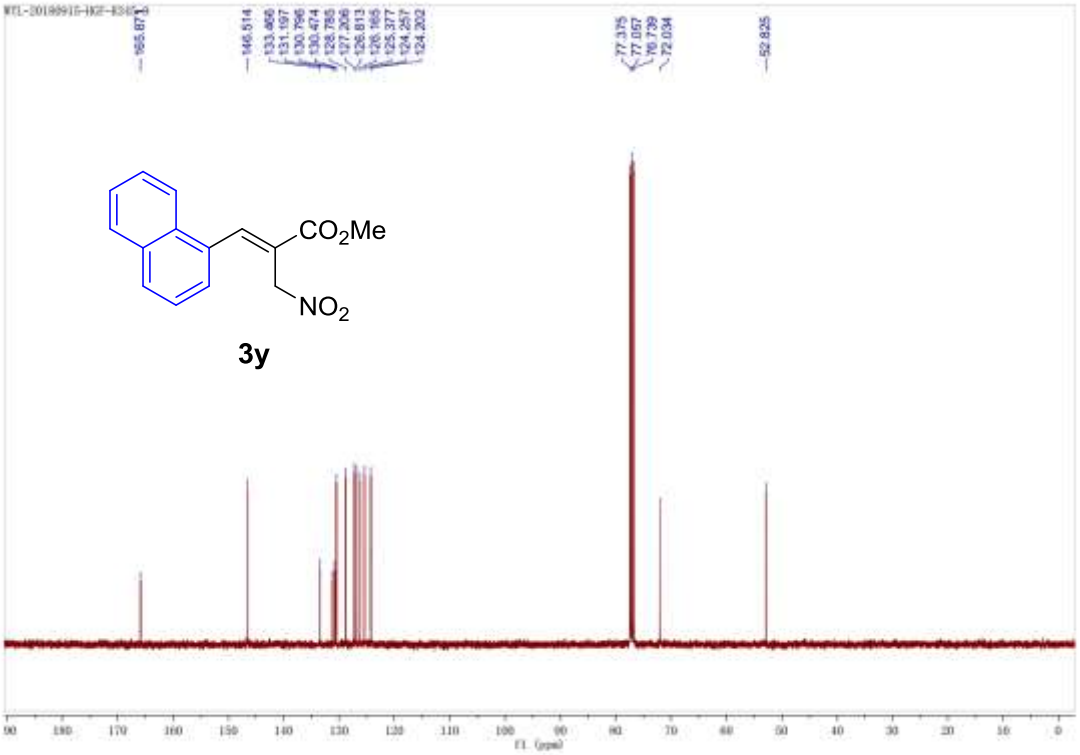

MeO
CO2Me
NO2
OMe
3w

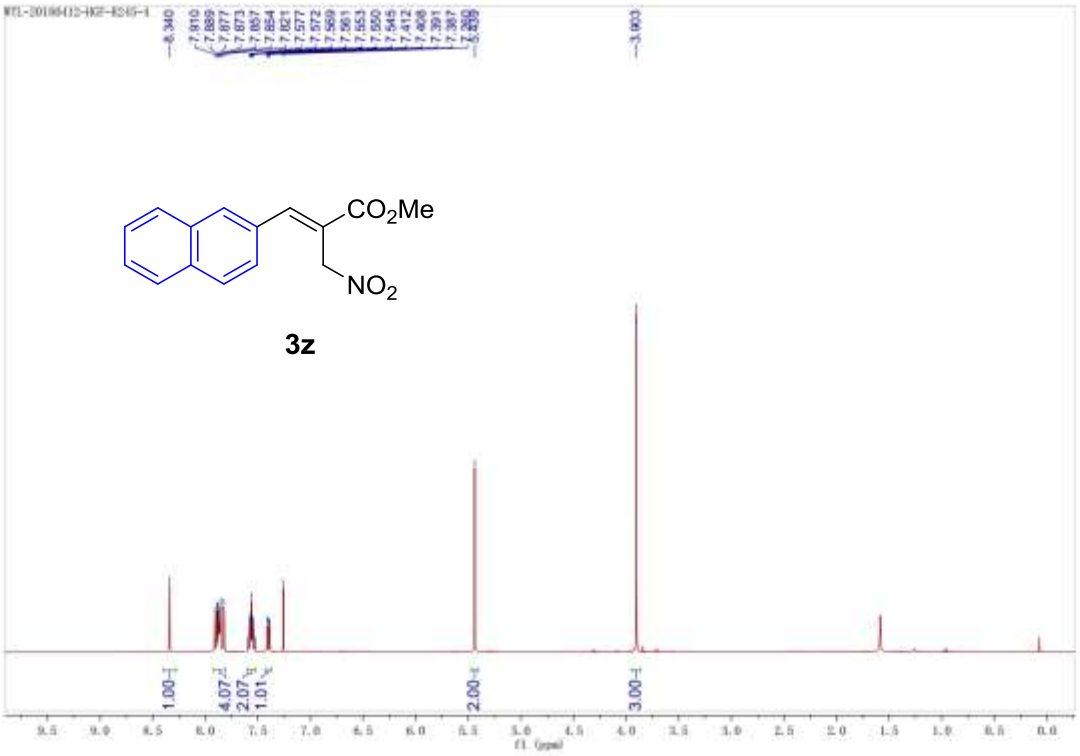

MeO
CO2Me
NO2
OMe
3w


8.060
7.534
7.513
7.437
7.432
7.260
7.179
7.174
7.158
7.153
5.304
3.875
Cl
Cl
CO2Me
NO2
3x
1.00
1.03
0.99
1.02
2.05
3.06
f1 (ppm)

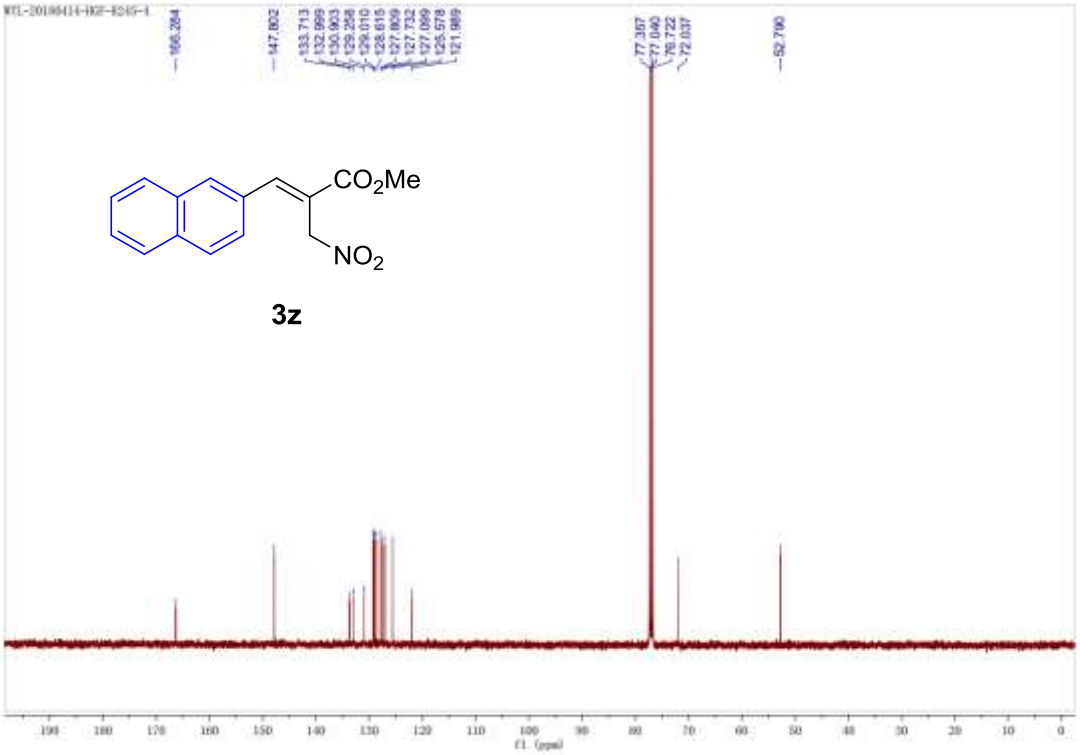

165.596
144.906
134.670
133.659
133.258
131.224
130.681
127.768
123.599
77.354
77.036
76.719
71.470
52.964
Cl
Cl
CO2Me
NO2
3x
f1 (ppm)


CO2Me
NO2
3y

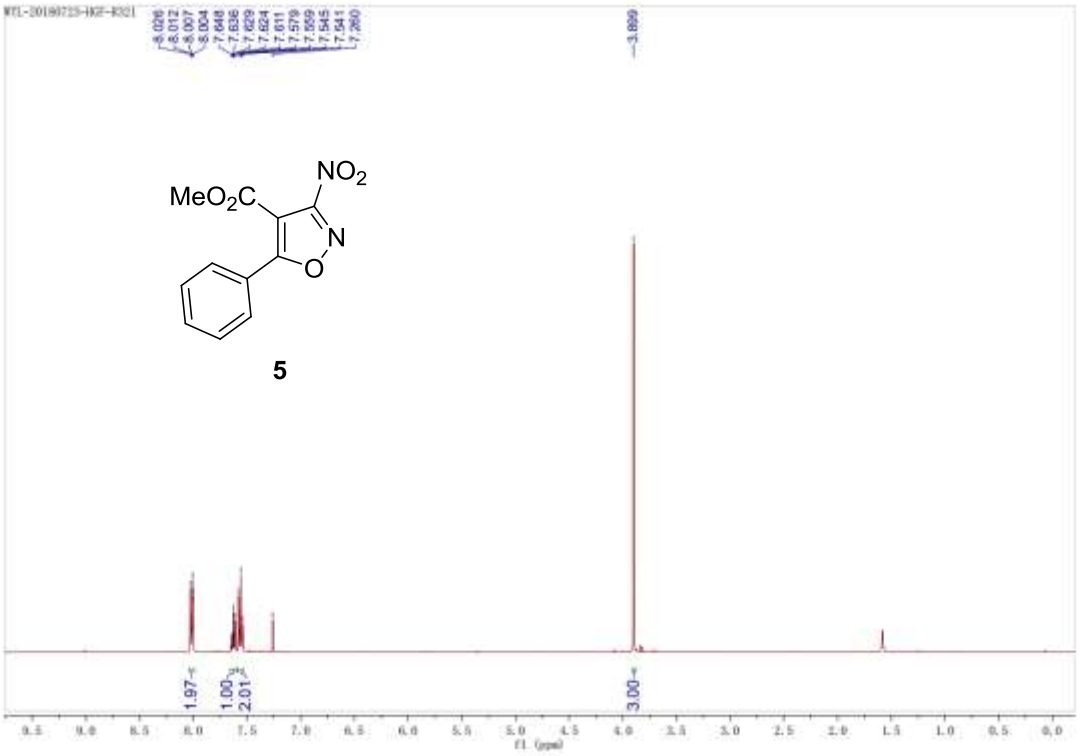

CO2Me
NO2
3y

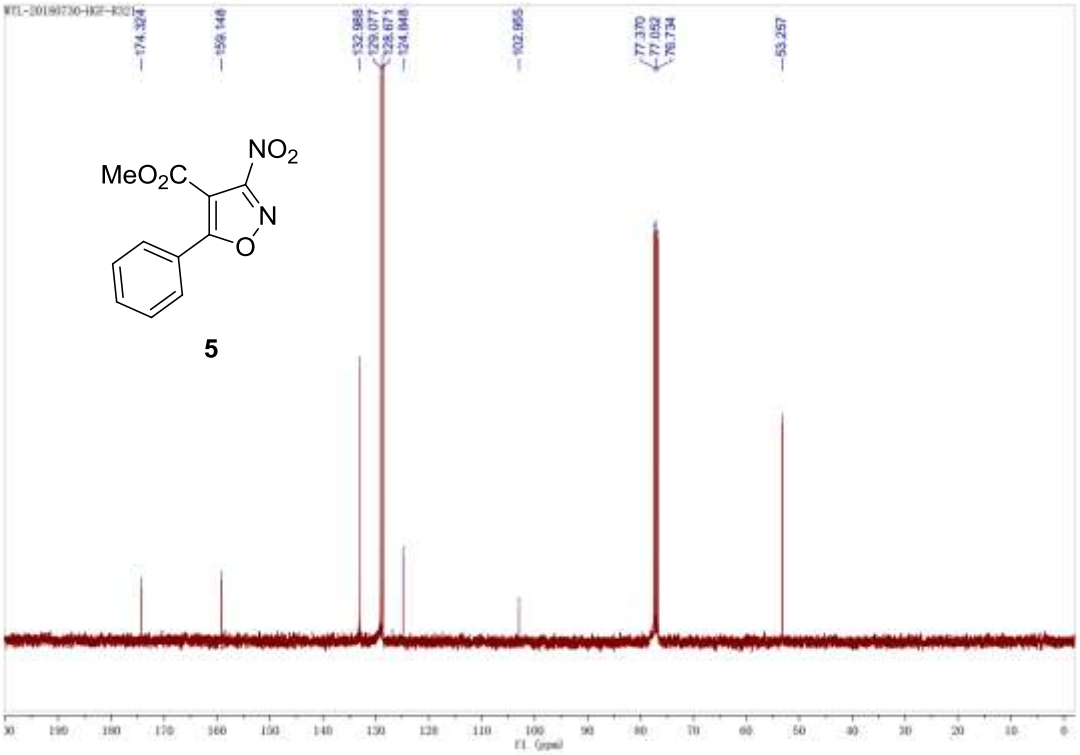

8.340
7.910
7.889
7.677
7.673
7.657
7.654
7.621
7.577
7.572
7.569
7.561
7.553
7.550
7.545
7.412
7.408
7.391
7.367
7.359
5.439
3.903
CO2Me
NO2
1.00
4.07
2.07
1.01
2.00
3.00
f1 (ppm)

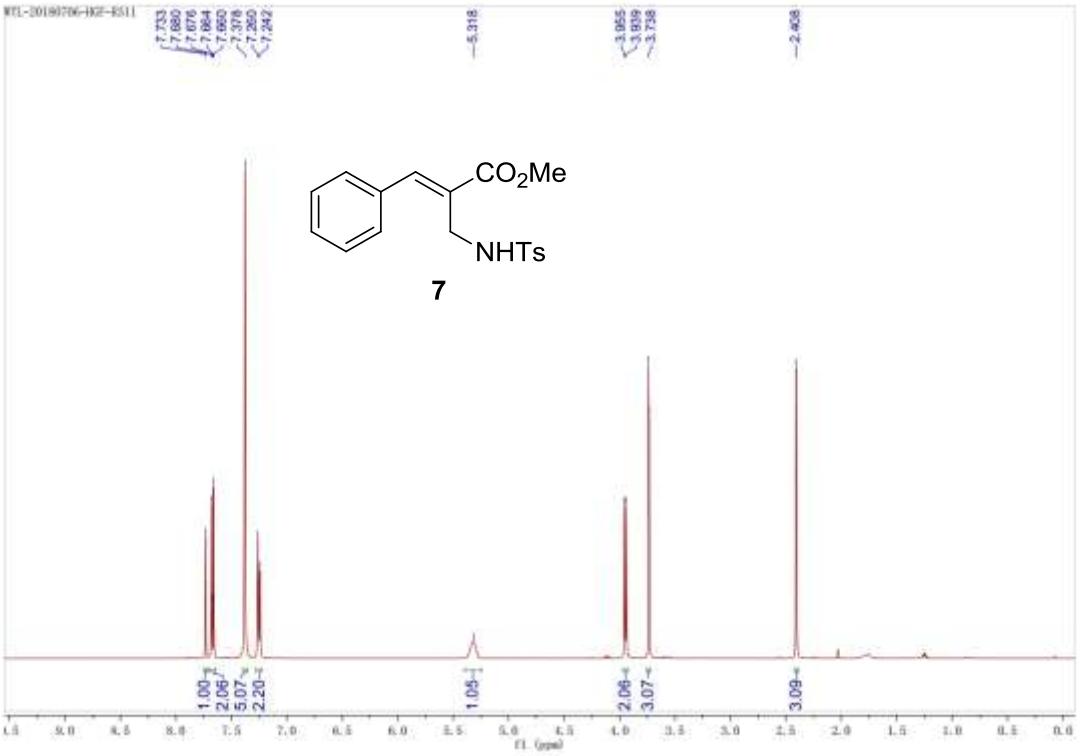
3z

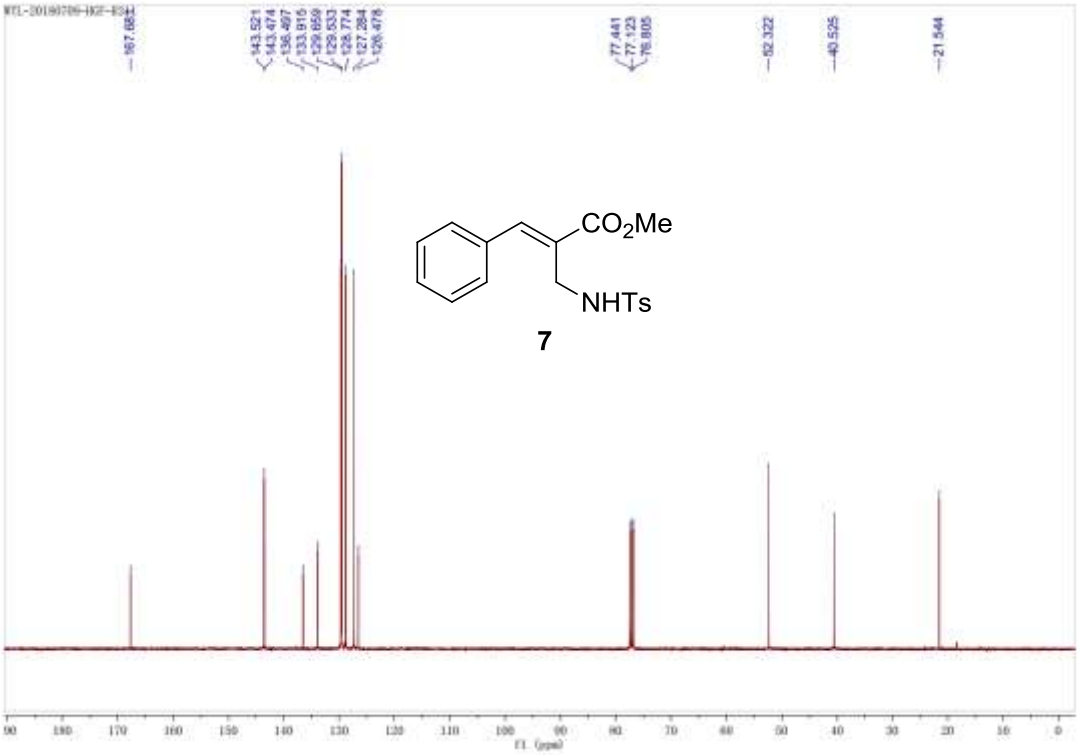

166.284
147.802
133.713
132.999
130.903
129.238
129.010
128.615
127.809
127.732
127.099
125.578
121.989
77.357
77.040
76.722
72.037
52.790
CO2Me
NO2
f1 (ppm)

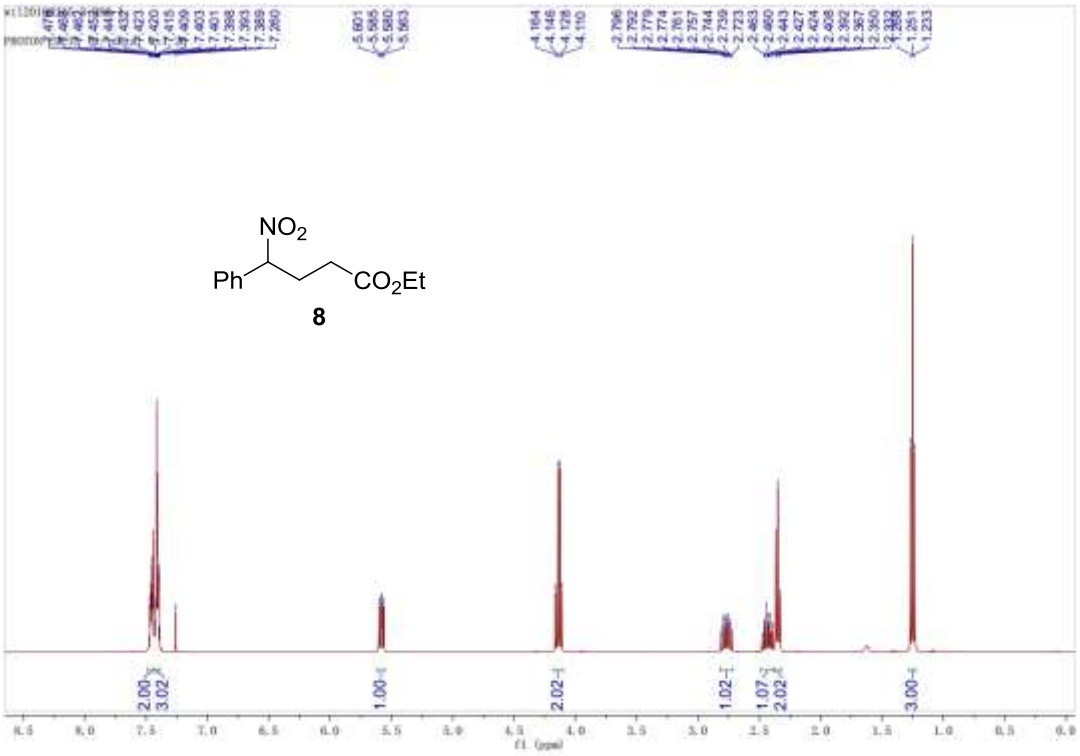
3z

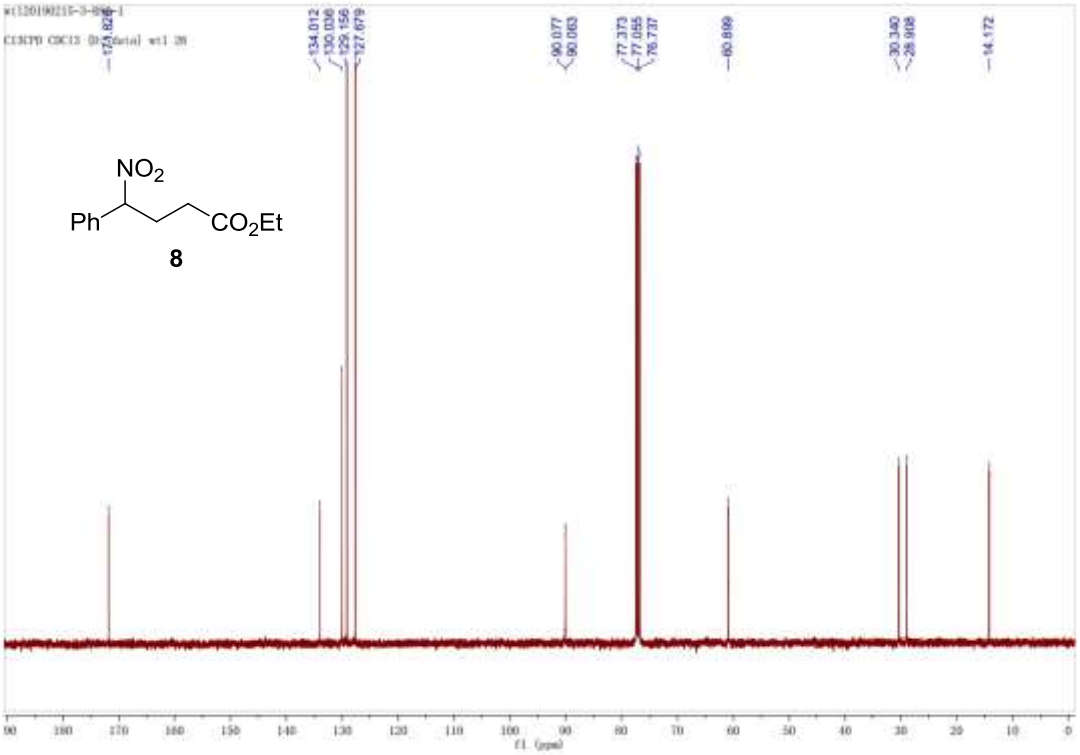

8.026
8.012
8.007
8.004
7.648
7.636
7.629
7.624
7.611
7.579
7.559
7.545
7.541
7.260
3.899
NO2
MeO2C
N
O
5
1.97
1.00
2.01
3.00
f1 (ppm)

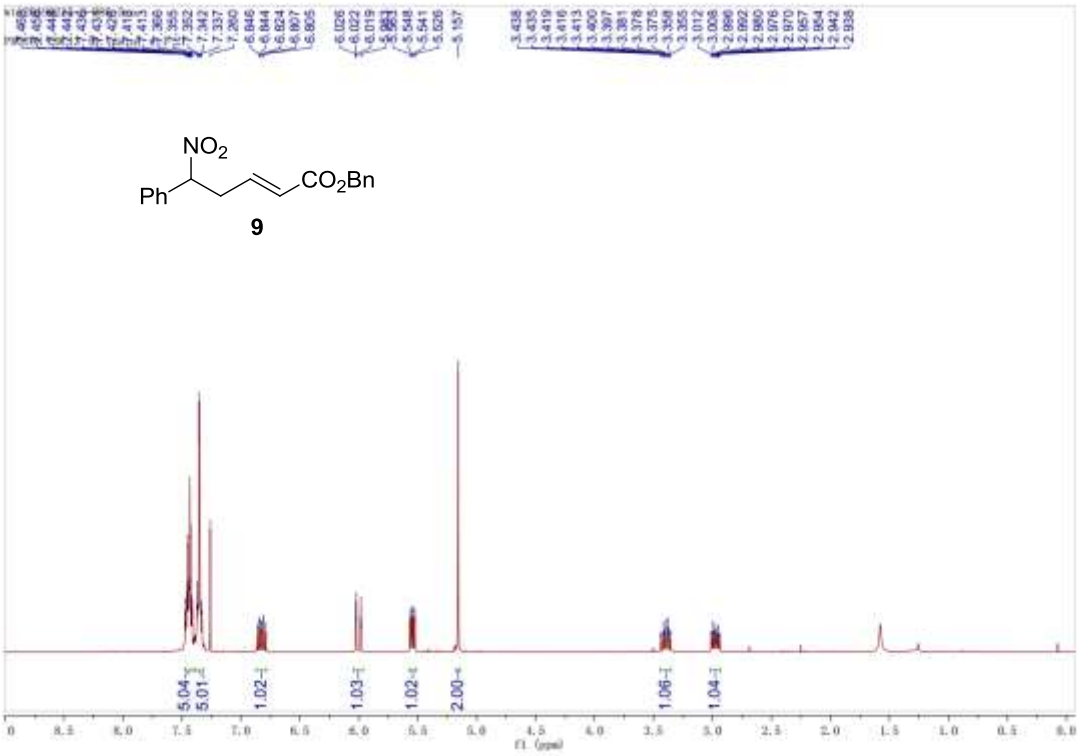

174.324
159.148
132.988
129.077
128.671
124.848
102.955
77.370
77.052
76.734
53.257
NO2
MeO2C
N
O
5
f1 (ppm)

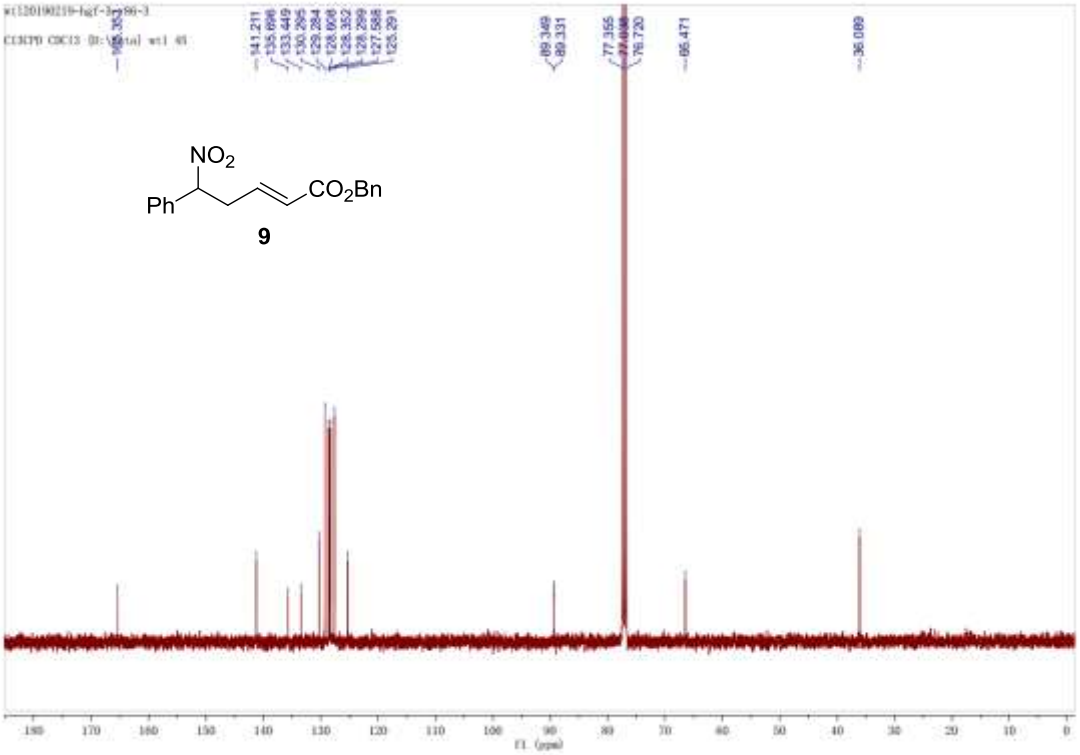

7.733
7.680
7.676
7.664
7.660
7.378
7.260
7.242
5.318
3.955
3.939
3.738
2.408
CO2Me
NHTs
7
1.00
2.06
5.07
2.20
1.05
2.06
3.07
3.09

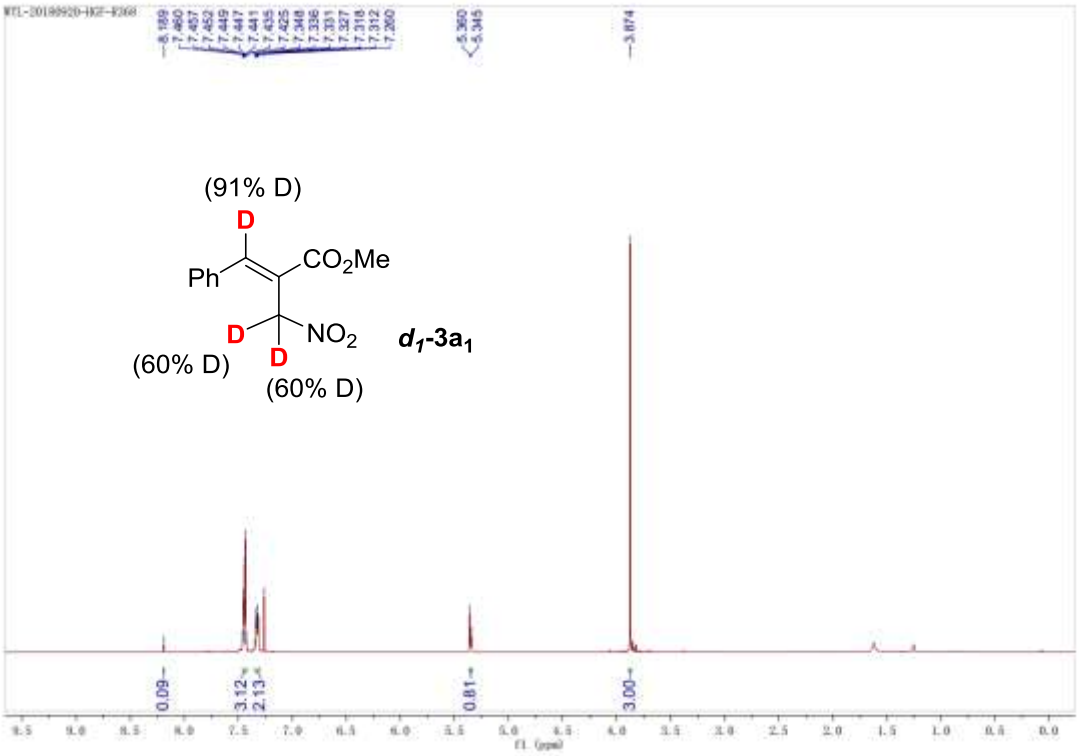

167.685
143.521
143.474
136.497
133.915
129.659
129.533
128.774
127.284
126.478
77.441
77.123
76.805
62.322
40.525
21.544
CO2Me
NHTs
7

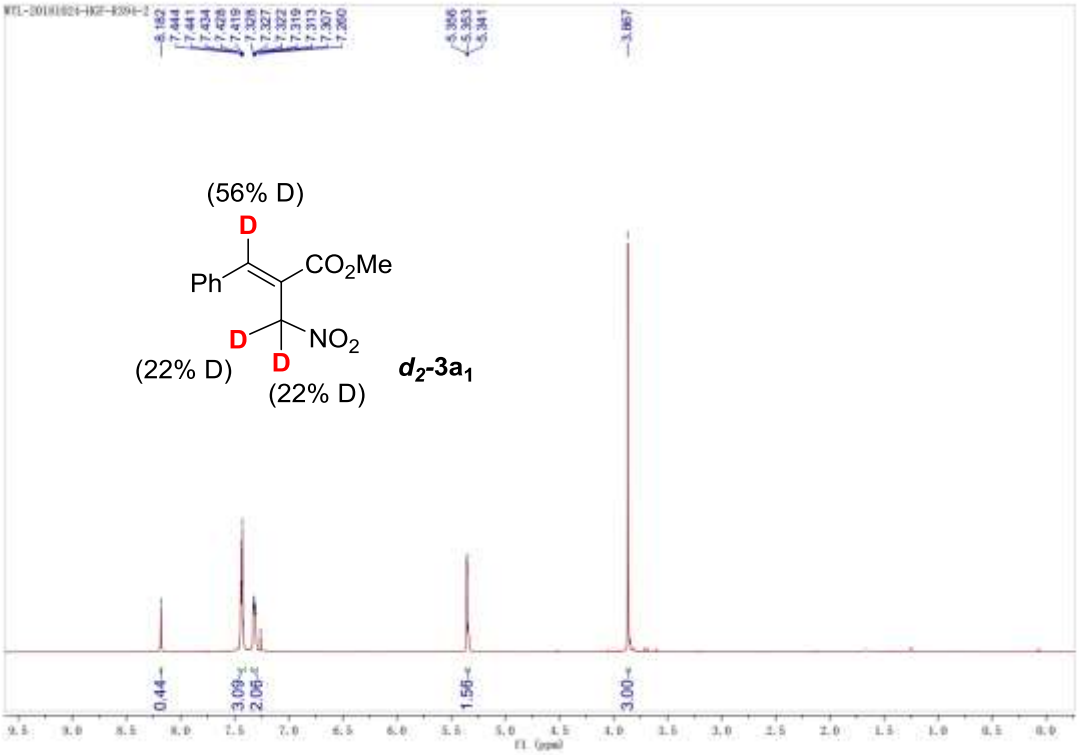

NO2
Ph
CO2Et
8

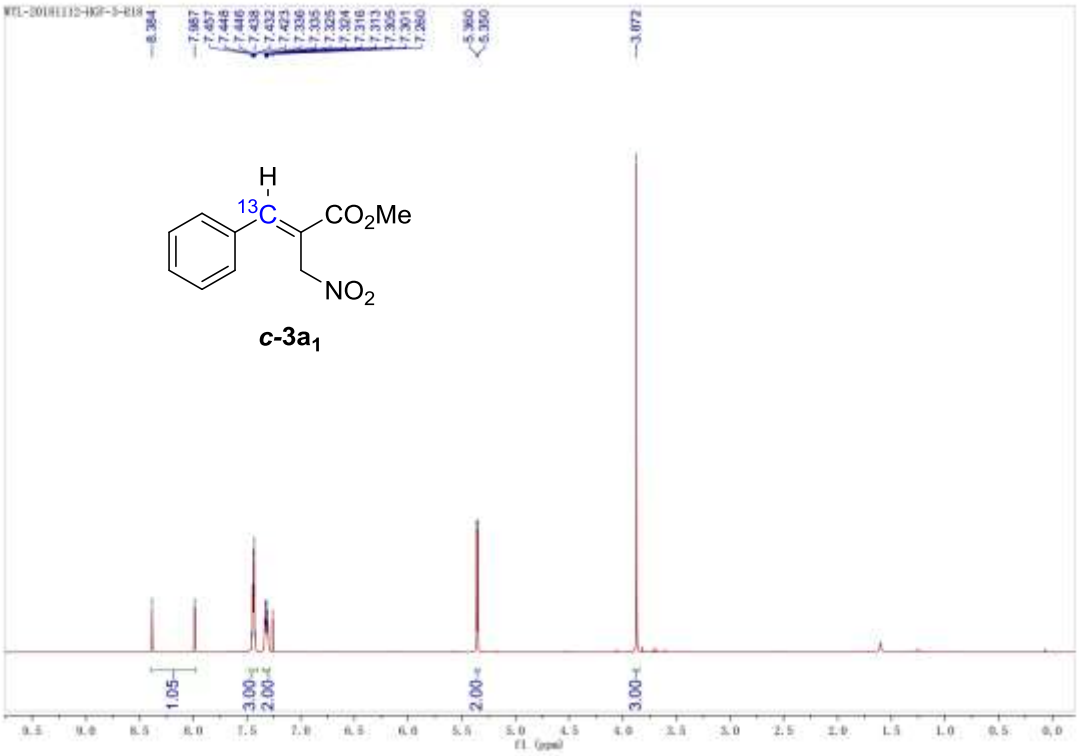

NO2
Ph
CO2Et
8


NO2
Ph
CO2Bn
9


NO2
Ph
CO2Bn
9


(91% D)
D
Ph
CO2Me
D
NO2
D
(60% D)
(60% D)
d1-3a1


(56% D)
D
Ph
CO2Me
D
NO2
D
(22% D)
(22% D)
d2-3a1


8.384
7.987
7.457
7.448
7.446
7.438
7.432
7.423
7.336
7.335
7.325
7.324
7.316
7.313
7.305
7.301
7.280
5.360
5.350
3.072
H
13C
CO2Me
NO2
1.05
3.00
2.00
2.00
3.00

***c*-3a$_1$**